FATTY TETRAZOLES AND OXAZOLINES

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CERTIFICATE

This is to certify that the work embodied in this dissertation entitled, "Fatty Tetrazoles and Oxazolines," is the original work of Mr. Rajiv Agarwal done under my supervision. The dissertation is suitable for submission for the award of the degree of Master of Philosophy in Chemistry.

Ahmad

(Dr. Mashood Ahmad)
Reader.

ACKNOWLEDGEMENTS

I have the proud privilege of working under the guidance of Dr. Mashood Ahmad. I owe him a deep sense of gratitude for this valuable supervision.

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Special thanks to my mother and brother who, as I believe will be the happiest sole on this earth to see my work completed.

Lastly I tender my thanks to ICAR-USDA project for granting a research fellowship.

(Rajiv Agarwal)

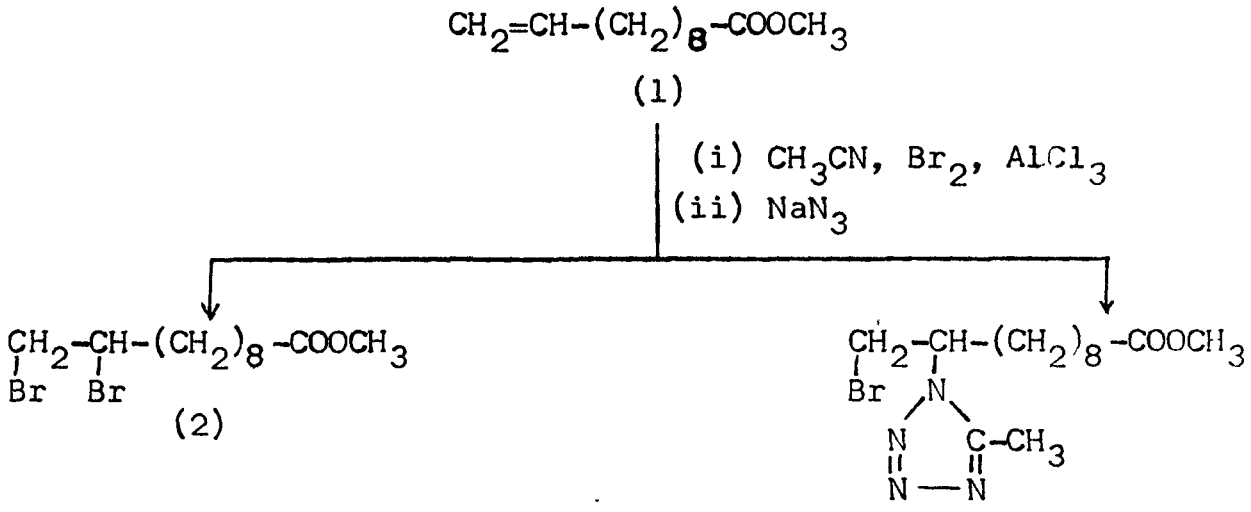
CONTENTS

SUMMARY

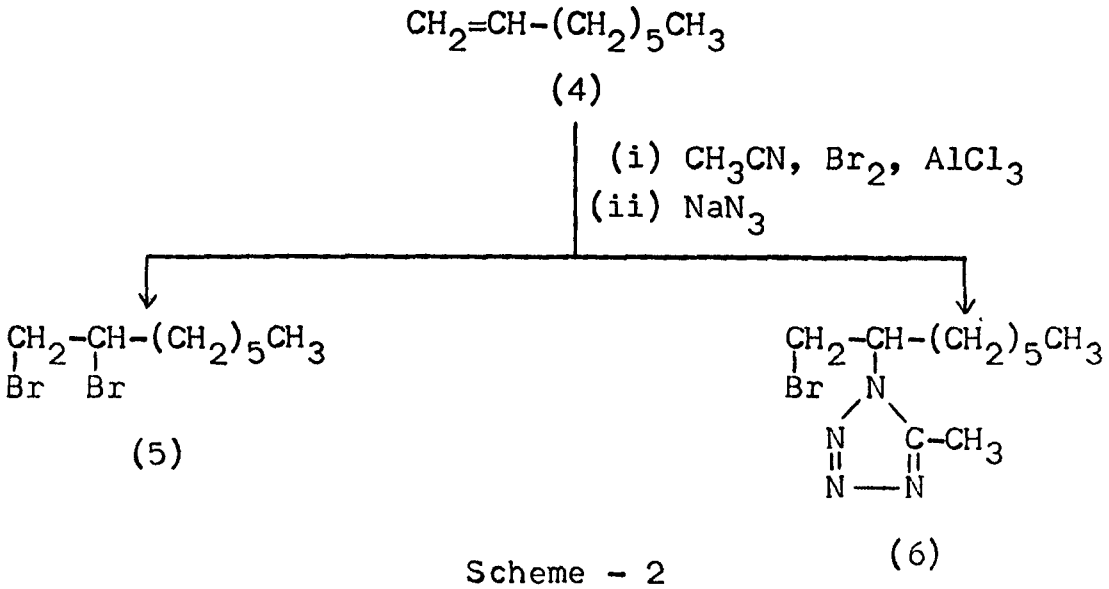
Results of the preparation of fatty tetrazoles, oxazolines and amides are recorded in this dissertation. The structures of the isolated compounds have been identified by spectral methods (IR, UV, NMR, MS). It is important to note that 2-oxazoline could not be prepared from 2,3-epoxyoctadecanoic fatty acid, whereas internal epoxy fatty ester did form this heterocycle.

Synthesis of Fatty Tetrazoles

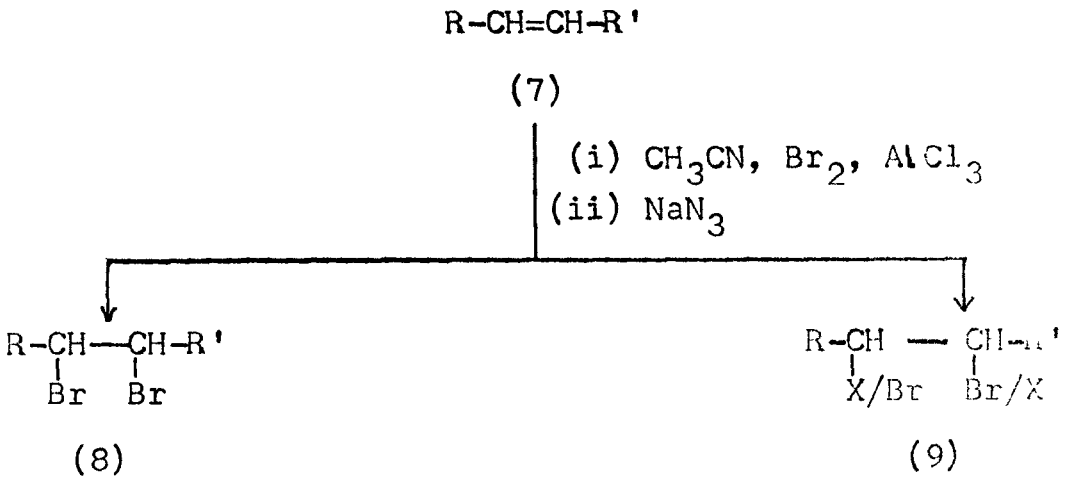
(1a) A tetrazole along with dibromo compound was obtained when methyl 10-undecenoate (1), 10-octene (4) and methyl cis-9,10-octadecenoate (7) reacted with bromine and sodium azide (NaN_3) in ethanenitrile (CH_3CN) in presence of aluminium trichloride ($AlCl_3$) [Scheme 1-3].



Scheme - 1

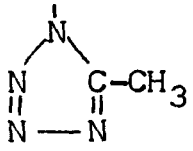


Scheme - 2



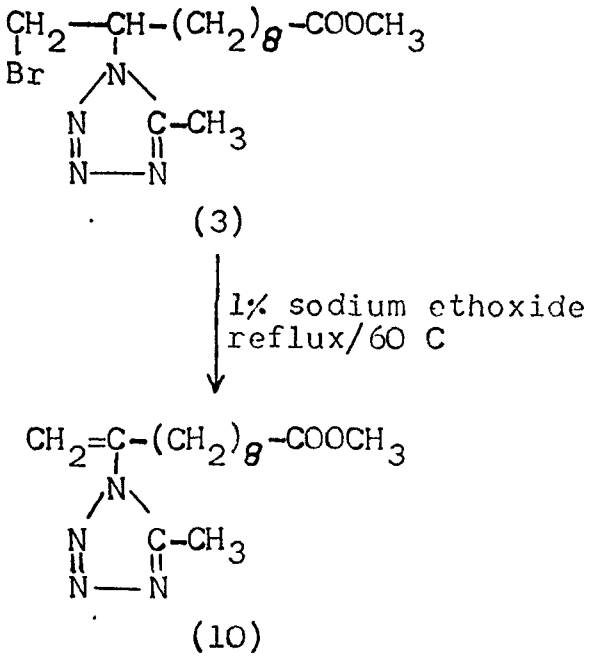
R = $CH_3-(CH_2)_7$

R'= $(CH_2)_7-COOCH_3$

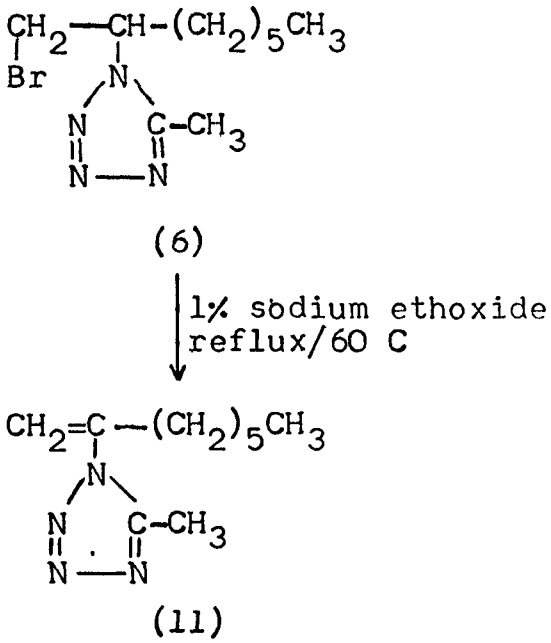
X = 

Scheme - 3

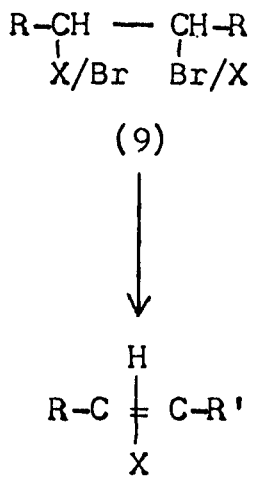
(1b) Bromo tetrazoles (3), (6) and (9) when refluxed with 1% sodium ethoxide at 60 C for 2 hours, resulted in the formation of dehydrobrominated tetrazoles (10), (11) and (12).



Scheme - 4



Scheme - 5

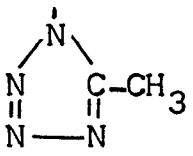


(9)

(12)

R = $CH_3-(CH_2)_7$

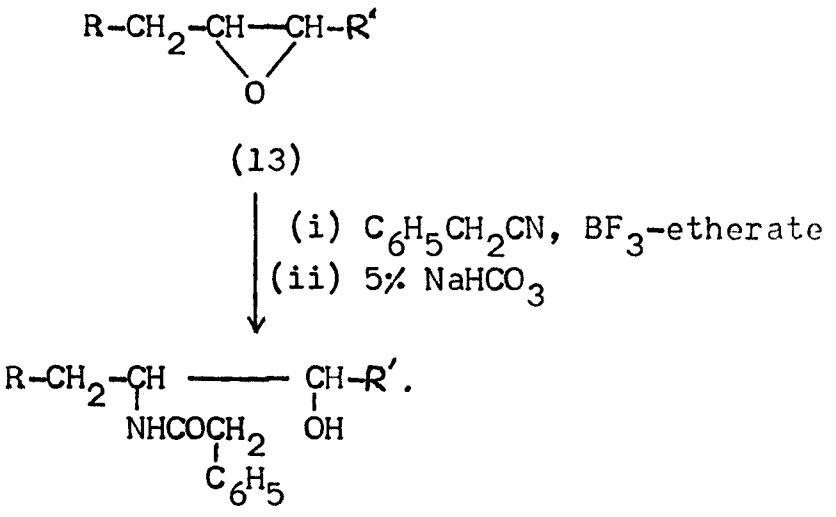
R'= $(CH_2)_7COOCH_3$

X = 

Scheme - 6

(2) Synthesis of Fatty 2-Oxazoline and Amides

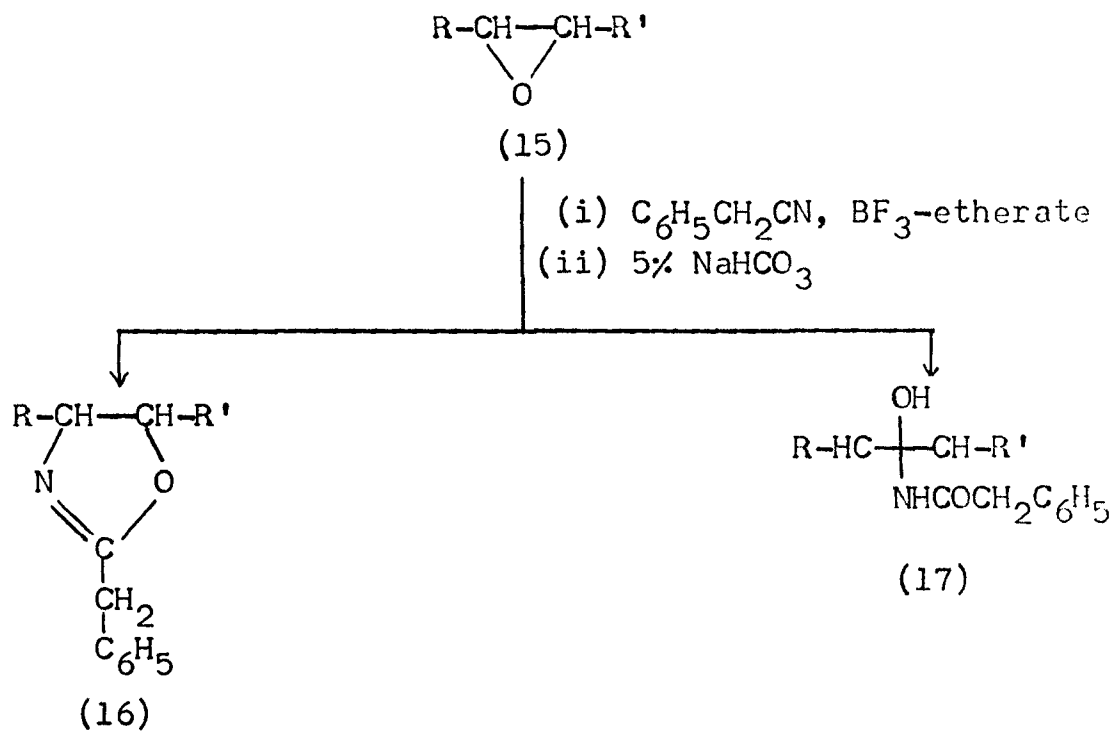
Long chain amides (14,17) and oxazoline (16) have been prepared from α,β-epoxy methyl ester (13) and 9,10-epoxy methyl ester (15), respectively. The reagent used in these preparation was benzylnitrile ($C_6H_5CH_2CN$) in presence of boron trifluoride-etherate (BF_3-etherate) [Scheme-7,8].



R = $CH_3-(CH_2)_{13}$

R'= $COOCH_3$

Scheme - 7



16,17 R = $CH_3(CH_2)_7$; R'= $(CH_2)_7COOCH_3$ and

R = $(CH_2)_7COOCH_3$; R'= $CH_3(CH_2)_7$

Scheme - 8

INTRODUCTION

The functionality of fatty acid molecules and their derivatives accounts for the utility of these materials in a large variety of applications. The increasing cost of petrochemicals has diverted the attention of chemists towards the synthesis of oleochemicals from natural fats and oils and their fatty acid derivatives. These fatty derivatives are becoming essential to a variety of industries such as coatings, surfactants, plasticizers, lubricants, additives, perfumes, insecticides and polymers. In nature, heterocyclic compounds such as alkaloids, vitamins and pigments are well known, long-chain fatty acids possessing a heterocyclic ring in the chain are a rarity in nature. However a few long chain substituted nitrogen[1] and oxygen[2] containing heterocyclic fatty acids are found in nature.

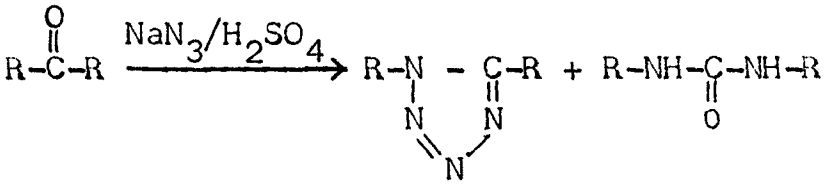
Tetrazoles[3,4] and oxazolines[5] have found important biological as well as nonbiological applications. Keeping in view the importance of these compounds, an affort was made to synthesise tetrazoles and 2-oxazolines. However it is surprising that all attempts failed to prepare 2-oxazoline from 2,3-epoxy fatty ester.

The present dissertation deals with the literature survey of tetrazoles and oxazolines, and preparation and characterisation of tetrazoles, 2-oxazolines and unusual products obtained.

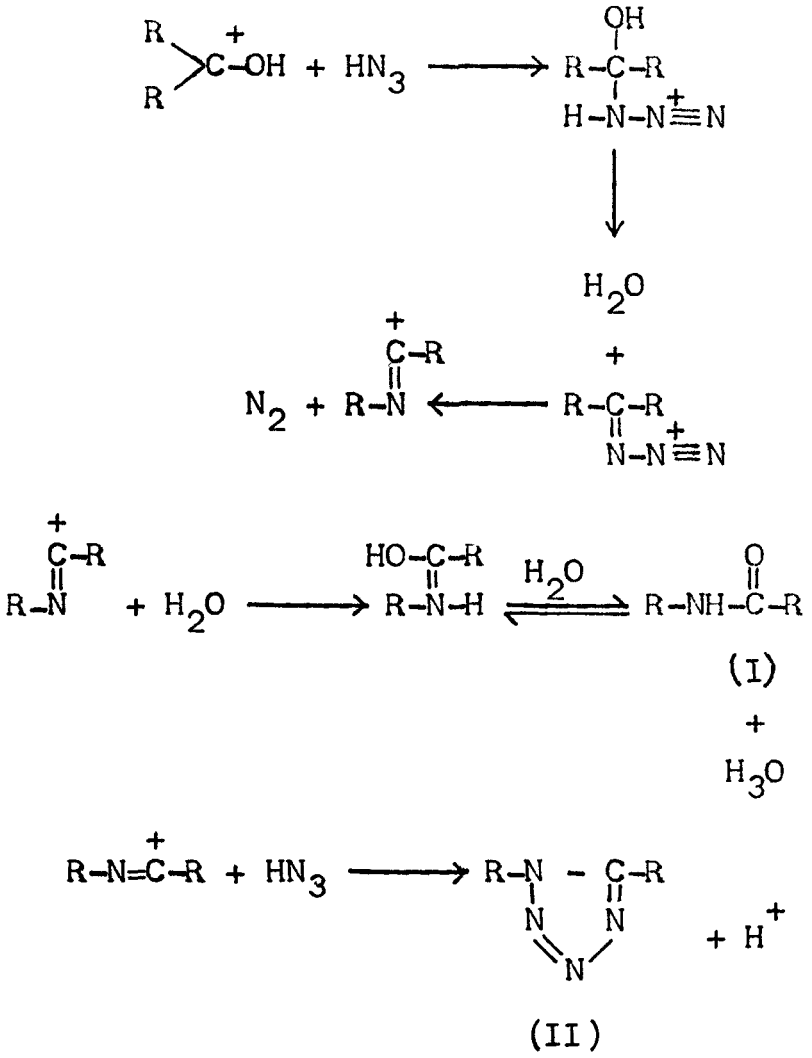
CHAPTER - I

TETRAZOLES

The five membered doubly unsaturated heterocycle with one carbon and four nitrogen atoms is known as tetrazole. The first tetrazole was recognised in 1885 by Bladin[6], during an investigation of dicyanophenylhydrazine. Treatment of dicyanophenylhydrazine with nitrous acid led to the formaton of a compound, which was characterised as 5-cyano-2-phenyltetrazole[7]. An excellent review, touching upon almost every aspect of tetrazole chemistry is due to Benson[4]. Reaction of a ketone with sodium azide (>2 mole), leads to the formation of tetrazole and urea derivatives.



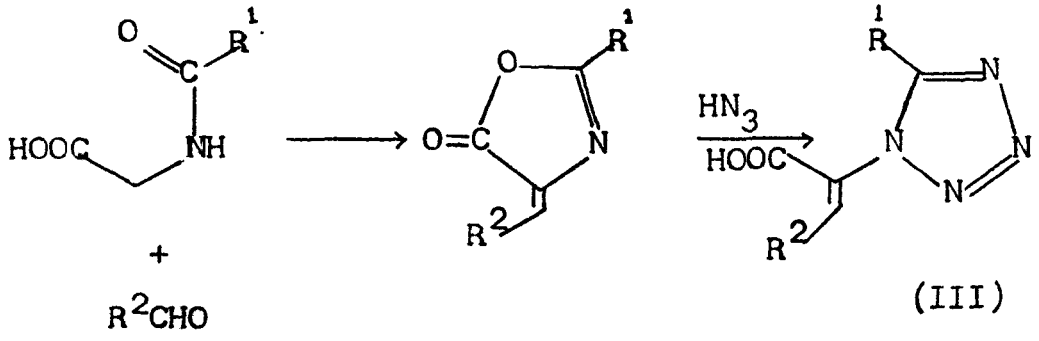
Schmidt[8] has reported the formation of tetrazole from acetone and diethylketone. Smith[9] critically examined the Schmidt reaction of ketones and developed a mechanism involving the formation of both amide (I) and tetrazole (II).



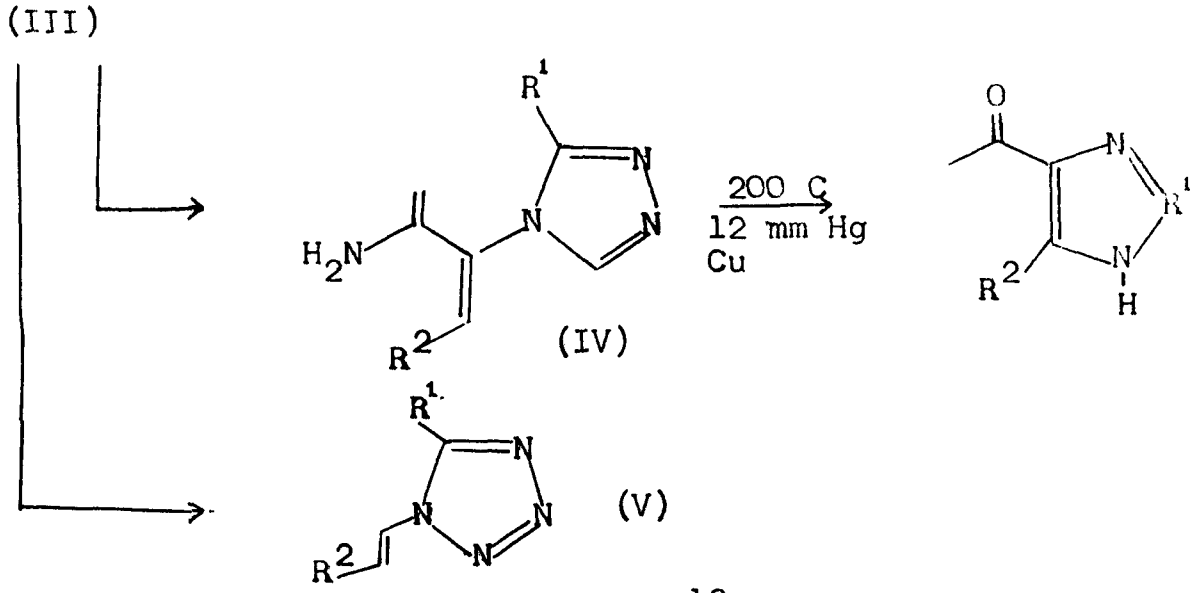
(I)

(II)

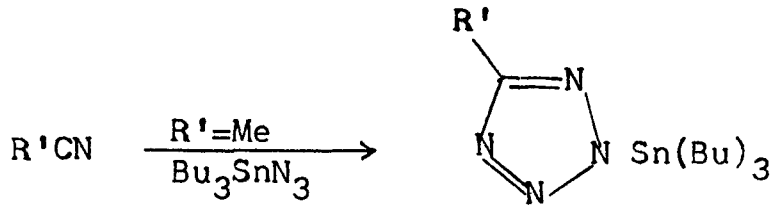
Four routes to 1-alkenyltetrazoles have been reported. The commonly used method involves the azidolysis of azlactones to give tetrazol-1-ylacrylic acid[10-12] (III).



(III)

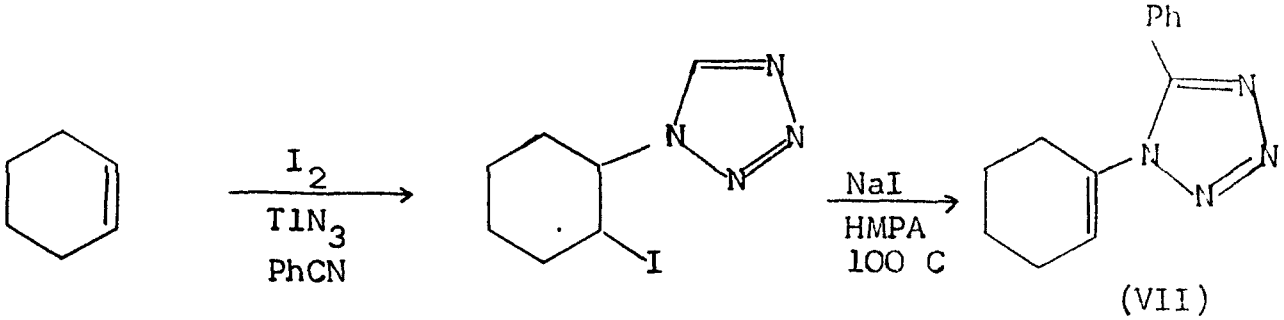


2-Tributylstannyltetrazoles[13] (VI) were synthesised by using alkyl or phenylcyanide and tributylstannylazide.



(VI)

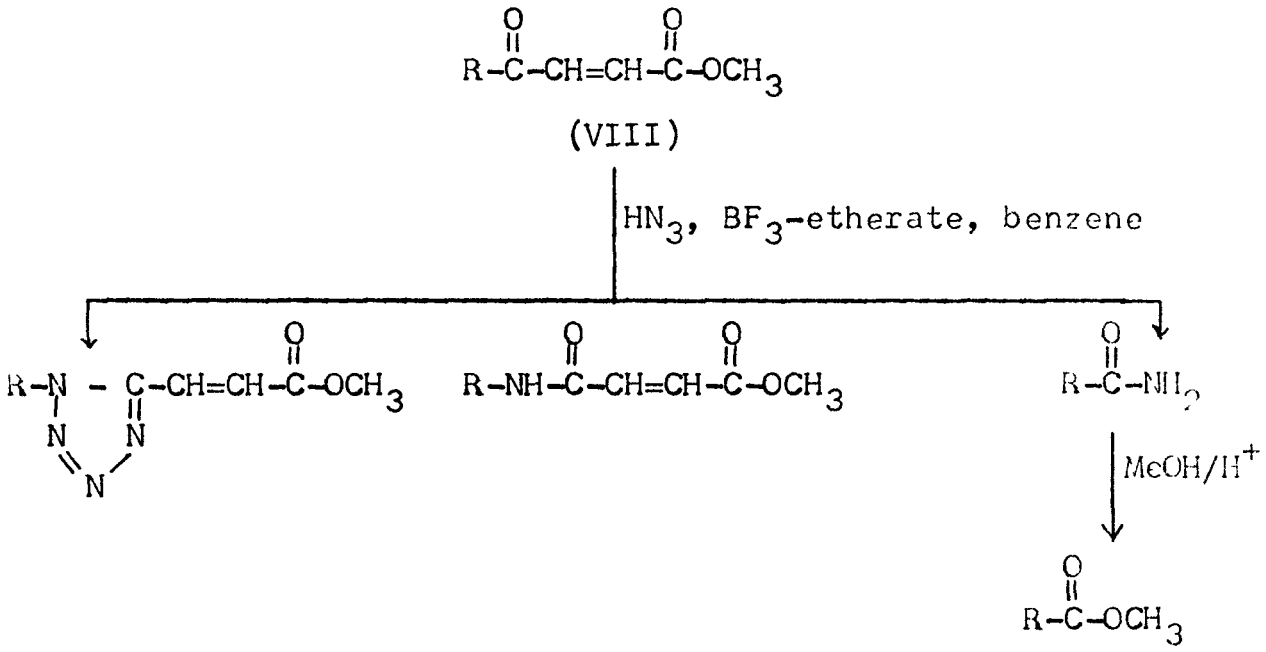
The cyclohexenyltetrazole (VII) was also prepared by an alternative but less satifactory route. Reaction of cyclohexene with iodine and thallium azide in benzonitrile[14] gave the iodocyclohexyltetrazole in low yield.



(VII)

HMPA = Hexamethylphosphoramide

In our laboratory[15] the fatty tetrazoles along with other products were synthesised by the reaction of methyl-4-oxo-trans-2-octadecenoate (VIII) on treatment with excess of hydrazoic acid at room temperature.



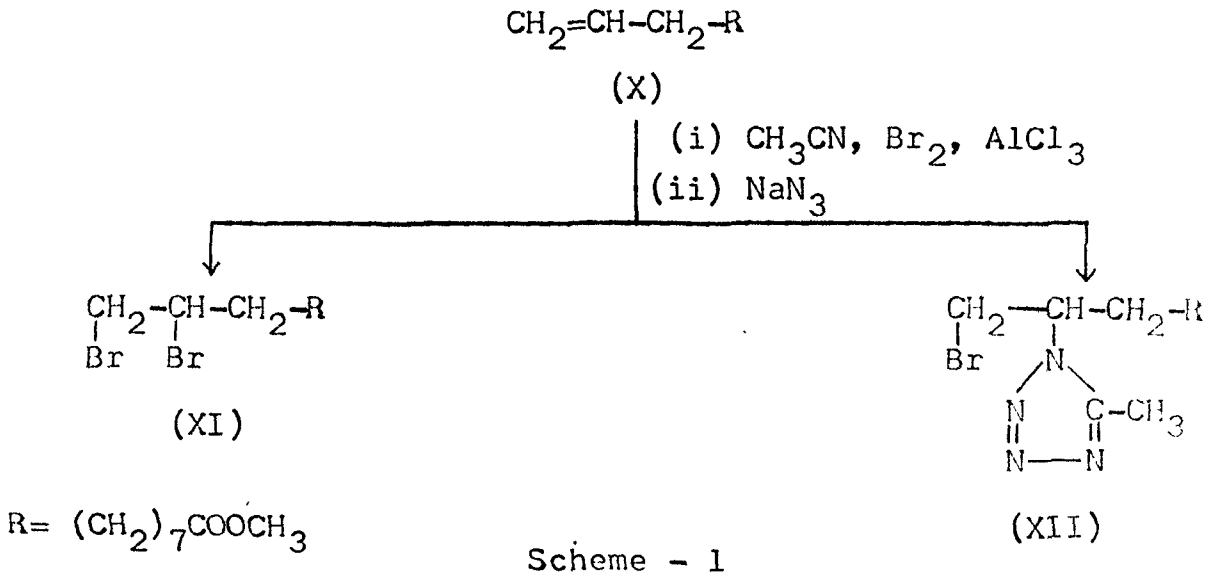
Tetrazoles have found important biological as well as nonbiological applications[3,4]. On nonbiological side they are of use in fibre, dyestuff and textile industries and have applications in photography also. On biological side, they are potent stimulants of the central nervous system and are used clinically to counteract intoxication due to over-dosage to barbiturates[3]. Stimulant depressent, sedative and analgesic activities are shown by certain tetrazoles. Anticonvulsant, hypotensive and andrenergic blocking actions are also exhibited by few tetrazole derivatives.

Present Work

Biological importance of tetrazoles has directed our attention towards the introduction of these heterocycles into long chain fatty compounds. In continuation of our study on fatty tetrazoles and with a view to introduce the tetrazole ring in fatty compounds through an easy route, we report here the reaction of bromine, ethanenitrile and sodium azide to some unsaturated fatty compounds (X, XIII, XVI) leading to tetrazole (XII, XV, XVIII, XIX, XX, XXI).

Reaction of Methyl 10-Undecenoate with Sodium Azide and Ethanenitrile

Methyl 10-undecenoate (X) on treatment with bromine and sodium azide in ethanenitrile at 0 C resulted in the formation of two compounds (XI) and (XII) [Scheme-1].



Scheme - 1

Characterisation of the Compound (XI)

The compound (XI) gave positive Beilstein test for halogen. Its IR spectrum exhibited characteristic bands at 1740 ($\underline{COO}CH_3$) and 670 (-CH-Br) cm^{-1}. The NMR spectrum of the compound gave signals at δ 4.4-3.95 m (3H, $-C\underline{H}_2$-Br and -C$\underline{H}$-Br), 3.75 s (3H, $COOC\underline{H}_3$), 2.2 m (2H, $C\underline{H}_2COO^-$) and 1.3 br s [14H, $(CH_2)_7$]. On the basis of these spectral data the compound (XI) was characterised as methyl 10,11-dibromoundecanoate.

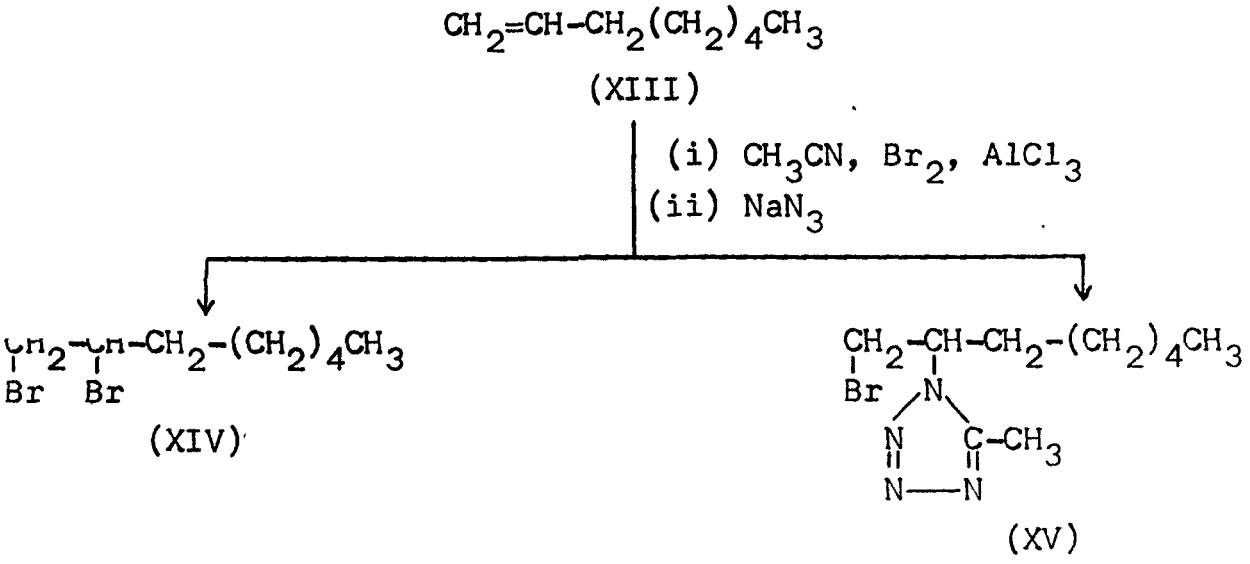
Characterisation of the Compound (XII)

The compound (XII) appeared to be a tetranitrogenous compound by its elemental analysis. The IR spectrum displayed bands at 1735 ($-\underline{COO}CH_3$), 1525, 1460, 1375 (N=N, C=N), 1235, 1080, 987 (CN_4 ring), 665 (CH-Br) cm^{-1} and UV spectrum showed a band at 215 nm due to tetrazole function[16]. The NMR spectrum of the compound gave conclusive information regarding the structure of tetrazole (XII). It exhibited peaks at δ 4.65 m (1H, C$\underline{H}$-N<), 3.9 s (1H) and 3.8 dist. d ($C\underline{H}_2$-Br, J=3 Hz), 3.6 s (3H, $COOC\underline{H}_3$), 2.61 s (3H, $\rangle C=C\underline{H}_3$), a multiplet centred at 2.3 4H, C-9 for methylene and α to carbonyl methylene protons, 1.28 br s (12H, chain-CH_2 signals). Thus the spectral data of the compound (XII) was assigned as methyl 1-bromo-2-(5'-methyl-1H-tetrazole) undecanoate.

Mass spectrum of (XII) further confirmed the structure by showing molecular ion peak at m/z 362/360 (M^+, 4). . The other prominent mass fragments were observed at 363/361 (M+1, 1.5) 280 (M-HBr, 55), 267 (M-CH_2Br, 9), 248 (280-CH_3OH, 66.7), 191/189 [M-$(CH_2)_8COOCH_3$, 7], 171 (M-$CH_2BrCN_4CH_3$, 4), 110 (191/189-Br, 78), 96 ($CH^+{=}CN_4CH_3$, 27), 95/93 (CH_2^+Br, 10), 84 ($CN_4CH_3+H^+$, 87).

Reaction of 1O-Octene (XIII) with Sodium Azide and Ethanenitrile

1O-Octene (XIII), when reacted with bromine and sodium azide at O C in ethanenitrile, afforded an oily compound. Fractionation of the reaction mixture over silica gel column gave two compounds (XIV) and (XV) [Scheme-2].



Scheme - 2

Characterisation of the Compound (XIV)

The compound (XIV) gave positive Beilstein test for halogen. Its IR spectrum gave a band at 668 (-C-Br) cm^{-1}. The NMR spectrum of the compound showed signals at δ 4.42-3.92 m (3H, $C\underline{H}_2Br$ and $C\underline{H}$-Br), 1.25 br s [1OH, $(CH_2)_5$], 0.90 dist. t. (3H, $C\underline{H}_3$). On the basis of the spectral data, the compound (XII) was formulated as 1,2-dibromooctane.

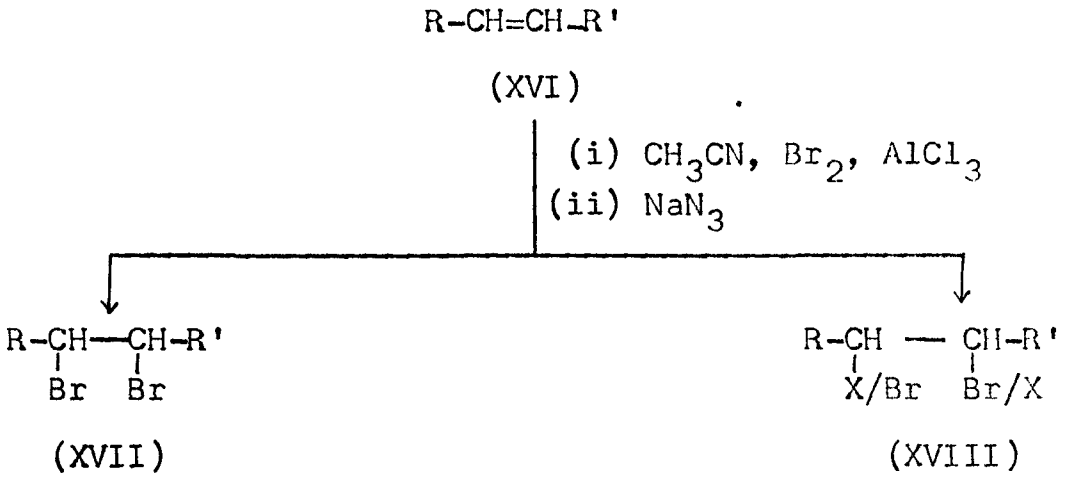
Characterisation of the Compound (XV)

It showed positive Beilstein test for halogen. The IR spectrum showed characteristic bands at 1525, 1455, 1380 (C=N, N=N), 1255, 1088, 985 (CN_4 ring), 665 (-C-Br) cm^{-1}. The UV of compound (XV) showed an absorption band at 215 nm, a characteristic of CN_4 ring. The NMR spectrum displayed significant signals at δ 4.71 m (1H, CH-N<), 3.91 s (1H) and 3.81 dist. d (1H, J=3 Hz) for $C\underline{H}_2$-Br, 2.61 s (3H, $\underset{\parallel}{\overset{\diagdown}{C}}$-$C\underline{H}_3$), 2.10 m (2H, C-3 methylene), 1.28 br s [8H, $(CH_2)_4$], 0.88 t (3H, CH_3).

Mass spectrum was more informative to confirm the structure of (XV). It gave some important fragmentation at m/z 277/275 (M+1, 1), 276/274 (M^+, 3), 194 (M-HBr, 60), 191/189 [M-$(CH_2)_5$-CH_3, 5], 179 (M-CH_2Br, 10), 95/93 (CH_2^+Br, 10), 85 (M-$CH_2BrCN_4CH_3$, 20), 84 ($CN_4CH_3+H^+$, 80). Thus the compound (XV) was shown to be 1-bromo-2(5'-methyl 1H-tetrazole)-octane.

Reaction of Methyl cis-9,10-octadecenoate (XVI) with Sodium Azide and Ethanenitrile

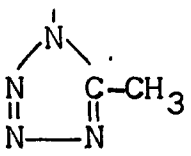
A 4 hour stirring of methyl cis-9,10-octadecenoate (XVI) in ethanenitrile at O C, in presence of bromine and sodium azide followed by column chromatographic separation on silica gel, afforded two compounds (XVII) and (XVIII) [Scheme-3].



R = $CH_3-(CH_2)_7$

R'= $(CH_2)_7-COOCH_3$

X =



Scheme - 3

Characterisation of the Compound (XVII)

The compound (XVII) gave a positive Beilstein test for halogen. The IR spectrum of (XVII) showed characteristic absorption bands at 1735 ($-\underline{COO}CH_3$), 665 (-C-Br) cm^{-1}. The NMR

spectrum showed the structure revealing signals at δ 4.21 m (2H, 2xC<u>H</u>-Br), 3.65 s (3H, COOC<u>H</u>$_3$), 2.2 m (2H, C<u>H</u>$_2$COO$^-$), 1.3 br s [26H, $(CH_2)_3$], 0.9 dist. t (3H, CH_3). Thus the compound (XVII) was formulated as methyl 9,10-dibromooctadecanoate.

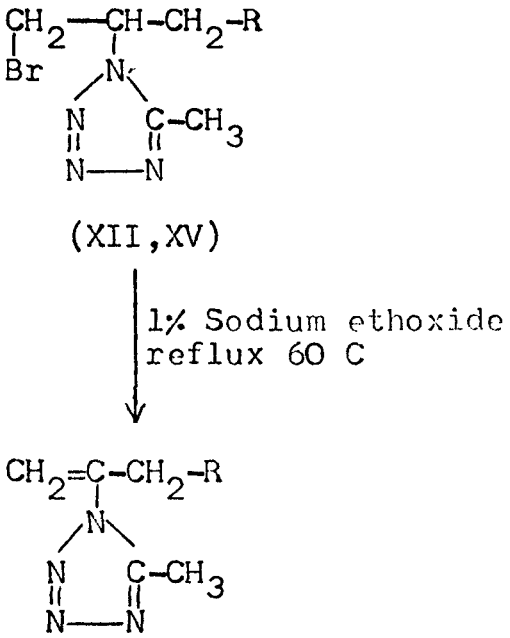
Characterisation of the Compound (XVIII)

The compound (XVIII) was shown to be halogenous by Beilstein test. IR of the compound (XVIII) gave the diagnostic bands at 1735 (C<u>O</u>OCH$_3$), 1535, 1465, 1375 (C=N, N=N), 1260, 1082, 985 (CN_4 ring), 665 (C-Br) cm^{-1}. The UV spectrum of the compound (XVIII) showed an absorption band at 215 nm, a characteristic of tetrazole ring. The NMR signals appeared at δ 4.49 m for the C-9 and C-10 methine protons to which the bromine and tetrazole ring are attached, 3.7 s (3H, COOC<u>H</u>$_3$), 2.59 s (3H, $\diagdown$C-CH_3), 2.21 m (4H, CH_2COO^-), 1.29 br s [24H, $(CH_2)_{12}$], 0.87 dist. t (3H, CH_3).

The conclusive support in favour of structure (XVIII) came from MS analysis and suggested the structure by showing characteristic fragmentation at m/z 461/459 (M+1, 1), 460/458 (M^+, 3), 378 (M-HBr, 38), 253 [M-$CH_3(CH_2)_7CHBr$, 10], 251/249 [M-$CH_3(CH_2)_7CHCN_4CH_3$, 13], 209 [M-$CHBr(CH_2)_7COOCH_3$, 18], 207/205 [M-$CH_3CN_4CH(CH_2)_7COOCH_3$, 14]. On the basis of mechanistic considerations and spectral data, the compound (XVIII) was formulated as methyl <u>threo</u>-9(10)-bromo, 10(9)-(5'-methyl 1H-tetrazole)-octadecanoate.

Reaction of (XII) and (XV) with Sodium ethoxide

Compounds (XII) and (XV) on refluxing with 1% sodium ethoxide for 2 hours, gave compounds (XIX) and (XX) in quantitative yields, respectively [Scheme-4].



XII,XIX,R = $(CH_2)_7-COOCH_3$

XV,XX,R = $(CH_2)_4CH_3$

Scheme - 4

Characterisation of Semi Solid Compound (XIX)

Its IR spectrum showed bands at 1735 ($\underline{COO}CH_3$), 1658, 922 (C=C), 1525, 1440, 1380 (C=N, N=N), 1271, 1085, 980 (CH_4 ring). Its UV spectrum gave the significant absorption band at 210 nm, due to the tetrazole ring. The NMR spectrum displayed characteristic signals at δ 5.4 dist. t (1H, J=1 Hz) and 5.21 s

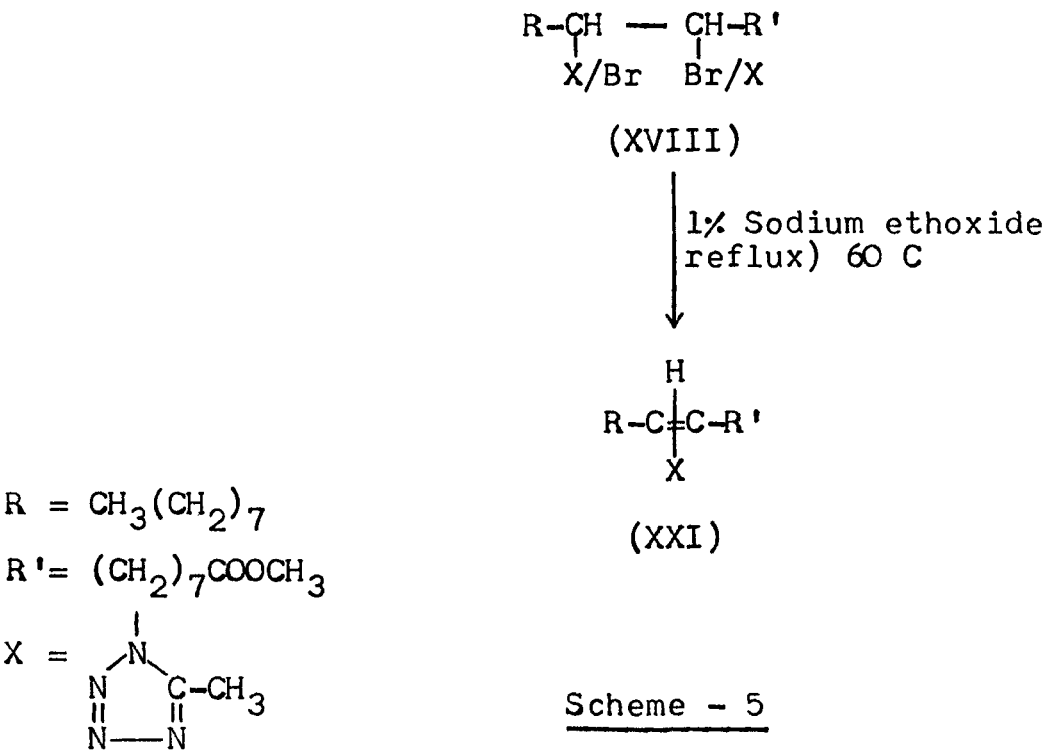
(1H for CH_2=C<), 3.58 s (3H, $COOCH_3$), 2.58 s (3H, >C-CH_3), 2.3 m (4H, CH_2COO^-), 1.28 br s [12H, $(CH_2)_6$]. All these spectroscopic data established the structure of (XIX) as methyl 10-(5'-methyl 1H-tetrazole)-undeca-10-enoate.

Characterisation of Oily Compound (XX)

In the IR spectrum of compound (XX) absorption bands were appeared at 1658, 915 (C=C), 1520, 1445, 1380 (C=N, N=N), 1275, 1088, 987 (CN_4 ring). The UV spectrum showed absorption at 210 nm, indicating the presence of tetrazole ring. The NMR spectrum of the compound showed structure revealing peaks at δ 5.4 dist. t (1H, J=1 Hz) and 5.29 s (1H for CH_2=C<, 2.54 s (3H, >C-CH_3), 1.28 br s [10H, $(CH_2)_5$], 0.88 dist. t (3H, CH_3). These data are in agreement with structure of the compound (XX) as 2-(5'-methyl 1H-tetrazole)-octa-1-ene.

Reaction of (XVIII) with Sodium ethoxide

The compound (XVIII) was refluxed with 1% sodium ethoxide at 60 C for 2 hours. The reaction mixture on usual workup yielded on oily compound (XXI). Which showed a single spot on TLC plate. However, theoretically the compound (XXI) should be an isomeric mixture [Scheme-5].



Scheme - 5

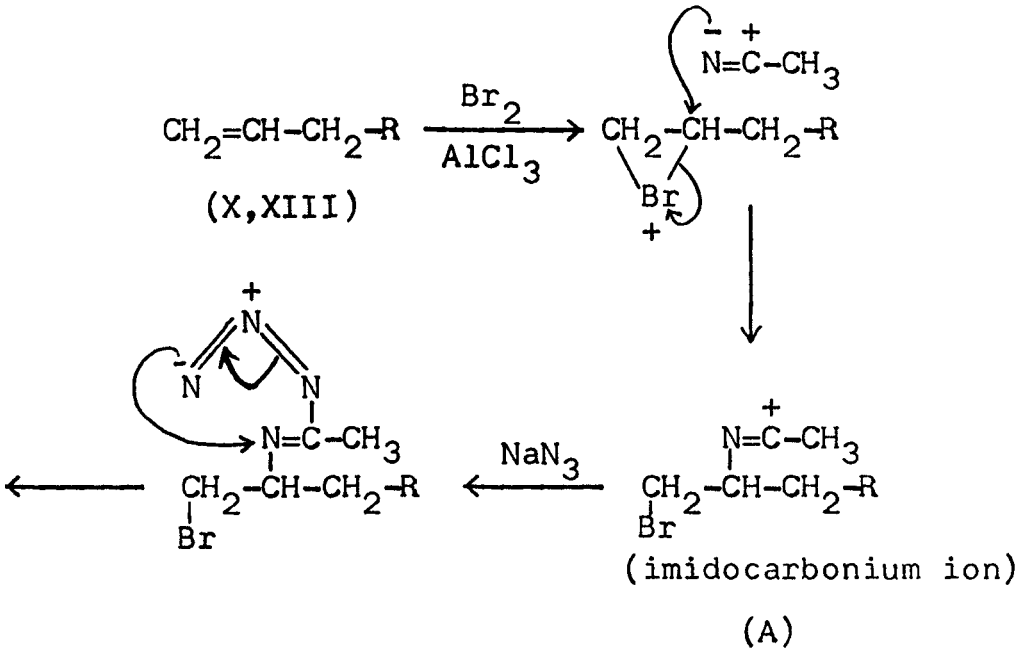
Characterisation of the Compound (XXI)

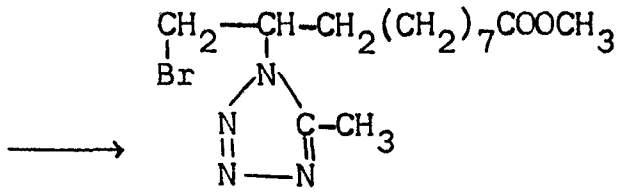
In its IR spectrum, absorption bands were appeared at 1740 (-COOCH$_3$), 1515, 1440, 1380 (C=N, N=N), 1278, 1080, 980 (CN_4 ring), 1670, 885 (C=C) cm^{-1}. Structure revealing band was shown by UV spectrum at 210 nm for tetrazole ring. The NMR spectrum exhibited diagnostic peaks at δ 5.88 t for the C-9 or C-10 methine protons to which the tetrazole ring is attached, 3.62 s (3H, -COOCH$_3$), 2.45 s (3H, C-CH$_3$), 2.3 m (4H, CH$_2$COO$^-$), 1.28 br,s [26H, $(CH_2)_{13}$], 0.87 dist. t (3H, CH$_3$). Thus the compound (XXI) was shown to be an isomeric mixture of methyl 9(10)-(5'-methyl-1H-tetrazole)-octadeca-9(E)-enoate. The assignment of E-geometry

was based on mechanistic approach (anti-elimination) and literature report[17].

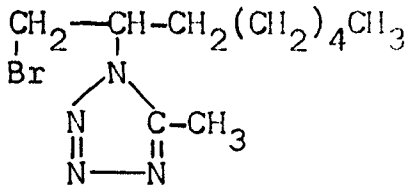
Mechanism for the Formation of Tetrazoles

Formation of compounds (XII,XV) from terminal olefinic acids (X,XIII) shows that the reaction is regiospecific. This involves the intermediacy of cyclic three membered bromonium ion intermediate[18]. The bromide ion and ethanenitrile which are present in reaction mixture may act as nucleophile. The bromide ion was made ineffective by the addition of anhydrous aluminium trichloride. Ethanenitrile opens the bromonium ion at the more substituted carbon leading to imidocarbonium ion (A). The ion(A) underwent cyclocondensation with sodium azide to afford tetrazoles. Threo-conformation of (XVIII) was designated on the basis of literature report[18] and mechanistic approach[19].





(XII)

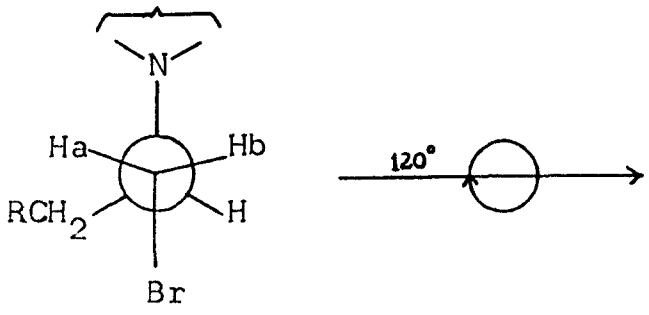


(XV)

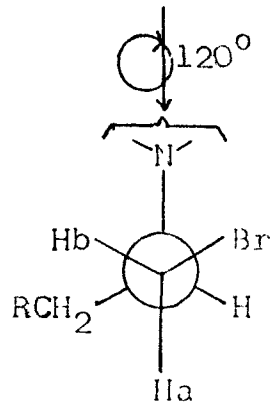
X, R= $(CH_2)_7COOCH_3$

XIII, R= $(CH_2)_4CH_3$

Methylene protons (Ha,Hb) attached to bromine in compounds XII and XV, are magnetically non-equivalent by virtue of their different stereochemistry. Therefore, they have a different chemical shift in their NMR spectrum.



(B) (C)



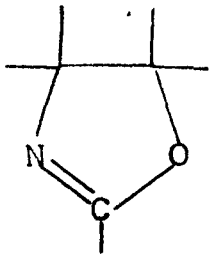
(D)

CHAPTER - II

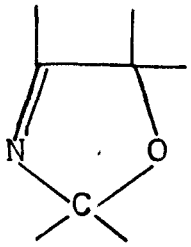
OXAZOLINES

Oxazolines have been known for their biological and industrial applications[20-30] and used frequently for the treatment of allergy, ulcers and hypertension etc., and also used in industries as moulding and coating composition.

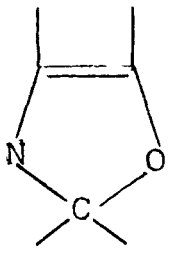
Oxazolines are five membered heterocyclic compounds having one double bond. The double bond may be located in one of the three positions, leading to the formation of three different oxazolines.



2-Oxazoline



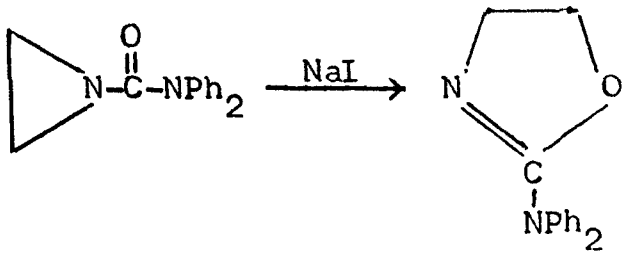
3-Oxazoline



4-Oxazoline

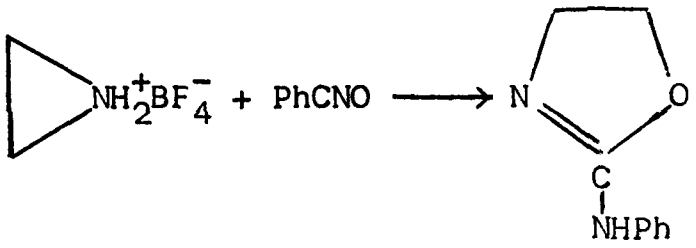
2-Oxazolines are most common, whereas the 3- and 4-oxazolines are very little in number.

Earlier, oxazolines have been prepared from amino-alcohols[31] and aziridines[32-34]. Aziridine derivatives[35,36] give a good yield of 2-diphenylamino-$\triangle^{2}$-oxazoline (XXII) when N,N-diphenyl-1-aziridine carboxamide is refluxed with acetone containing sodium iodide.



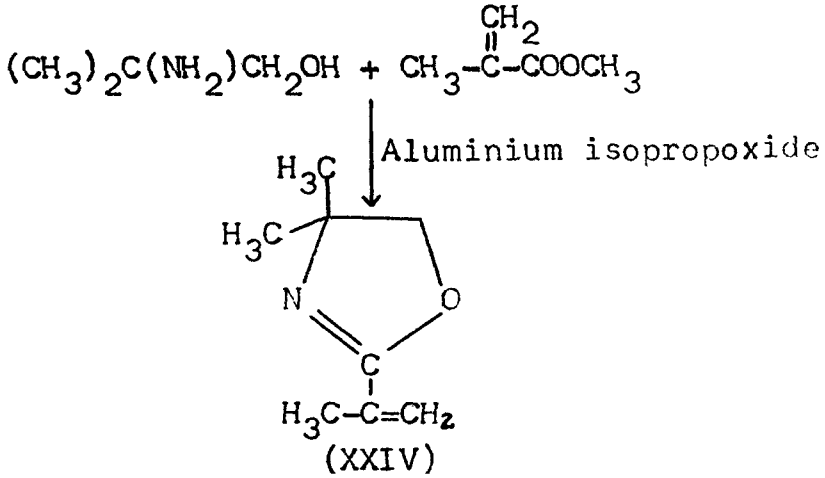
(XXII)

It has been reported[37] that the reaction of aziridinium tetrafluoroborate with phenylisocyanate gives good yield of 2-phenylamino-2-oxazoline (XXIII).



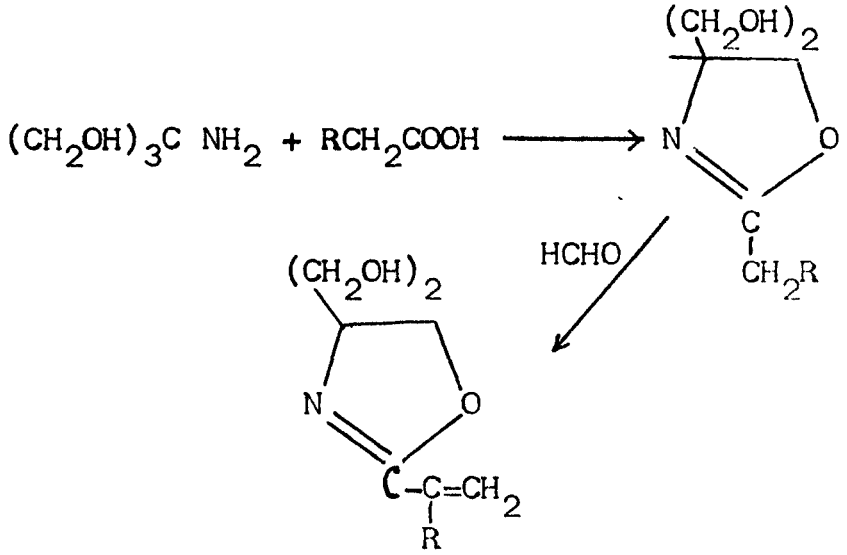
(XXIII)

Amino alcohols on reaction with acrylic esters give vinyl oxazoline[38-40]. 2-Amino-2-methyl-1-propanol and methyl methacrylate in presence of aluminium isopropoxide gives 2-isoprophenyl-4,4-dimethyl-2-oxazoline (XXIV).



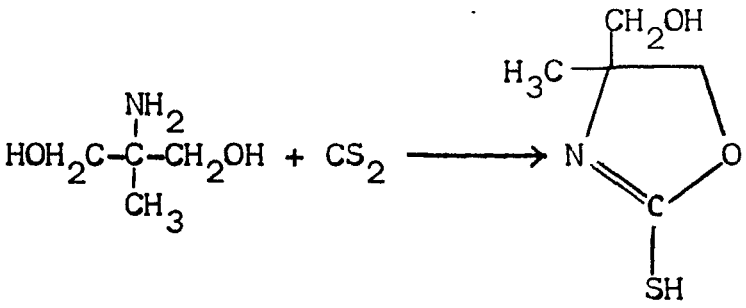
(XXIV)

Vinyl oxazoline (XXV)[41,42] can be prepared by the reaction of 2-amino-2-hydroxymethyl-1,3-propanediol and linseed oil fatty acid followed by the action of formaldehyde.



(XXV)

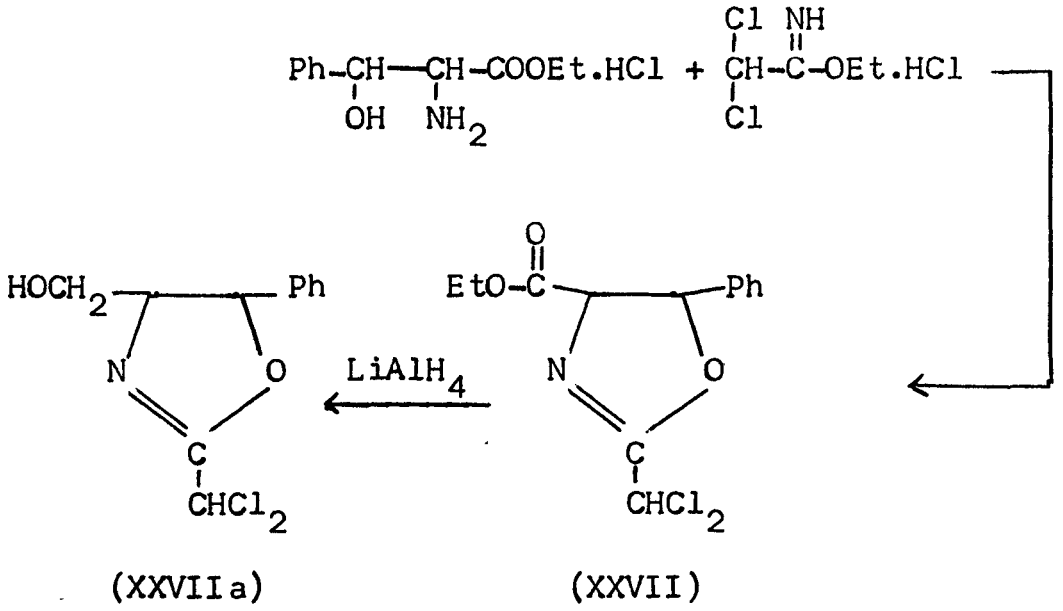
2-Mercapto-4-hydroxymethyl-4-methyl-2-oxazoline (XXVI) can be synthesised[43] by the reaction of carbondisulfide with 2-amino-2-methyl-1,3-propanediol.



(XXVI)

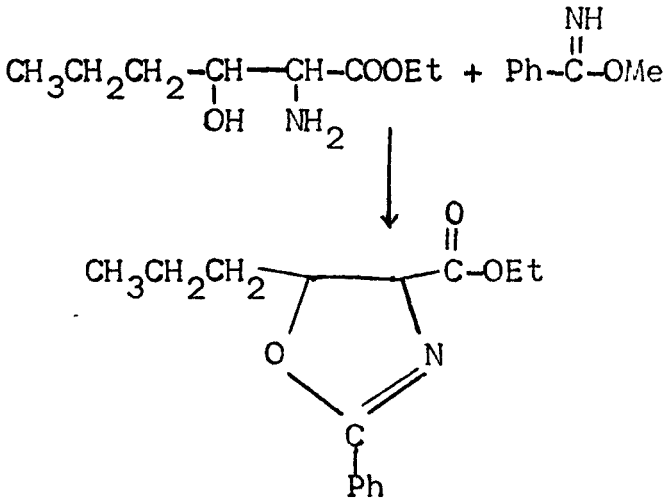
Chloromphenicol, an antibiotic, has a close resemblence with the chemistry of oxazoline[44]. The 4-hydroxymethyl

derivative of oxazoline has attracted a considerable interest. The best known reaction for the preparation of oxazoline is with β-phenylserine esters and ethyl 2,2-dichloroimido-acetate hydrochloride to form 2-dichloromethyl-4-carbethoxy-5-phenyl-2-oxazoline (XXVII), which can be converted to 4-hydromethyl derivative of oxazoline (XXVIIa)[45-51].



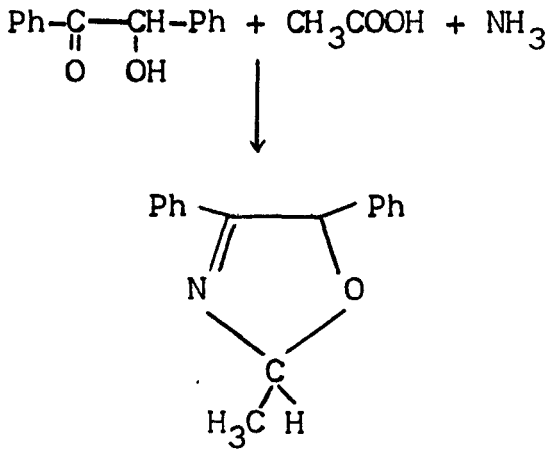
(XXVIIa) (XXVII)

cis-2-Phenyl-4-carbethoxy-5-propyl-2-oxazoline (XXVIII) has been obtained from the refluxing ethyl erythro-2-amino-3-hydroxy caproate hydrochloride with methylimidobenzoate, while trans-2-phenyl-4-carbethoxy-5-propyl-2-oxazoline has been obtained from the reaction of ethyl threo-2-amino-3-hydroxy-caproate[52].



(XXVIII)

A number of earlier[53], chemical procedures of 3-oxazolines were carried out by using several procedures of adding an α-hydroxyketone to acetic acid and ammonia. 2-Methyl-4,5-diphenyl-3-oxazoline (XXIX) was prepared in good yield by the action of benzoin in ethanol with acetic acid and gaseous ammonia.

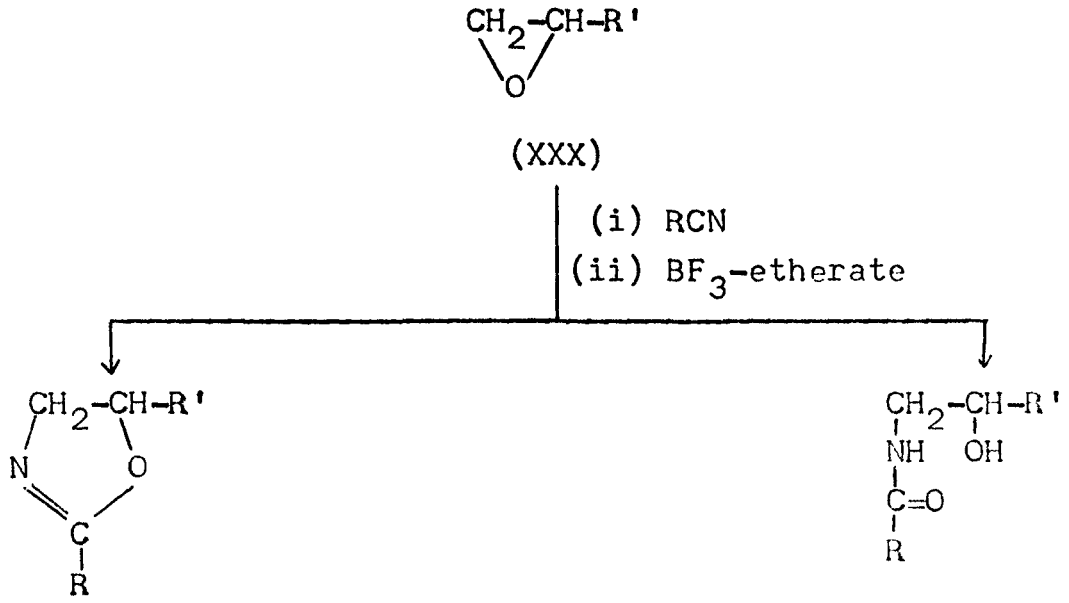


(XXIX)

Termnikava and Zhesko[54] have reported the condensation of α-methyl, α-phenyl and β-dimethylethylene oxide with benzonitrile in carbontetrachloride in the presence of $SnCl_4$ to gave a complex, which after treatment with aqueous NaOH gave 5,5-dimethyl-4-methoxy-2,4-diphenyl-2-oxazoline. Nerdel et al.[55] obtained 5-chloromethyl-2-(mono-di-tri)-fluoromethyl-2-oxazoline insatisfactoryyields from the appropriate fluorinated nitrile and 1-chloro-2,3-epoxypropane in the presence of tetraethylammonium chloride (TEAC).

The reaction of epoxides and nitrile provided an attractive approach to the synthesis of 2-oxazolines involving ring enlargement of epoxides. The use of epoxides as substrate and nitrile as reagent has been one of the most exploited method for the preparation of 2-oxazolines[56]. Oda et al.[57] were first to report this reaction using ethylene oxide and benzonitrile with conc. H_2SO_4 as catalyst. The compound was a mixture of 2,4-diethyl-2-oxazoline and 2,5-diethyl-2-oxazoline.

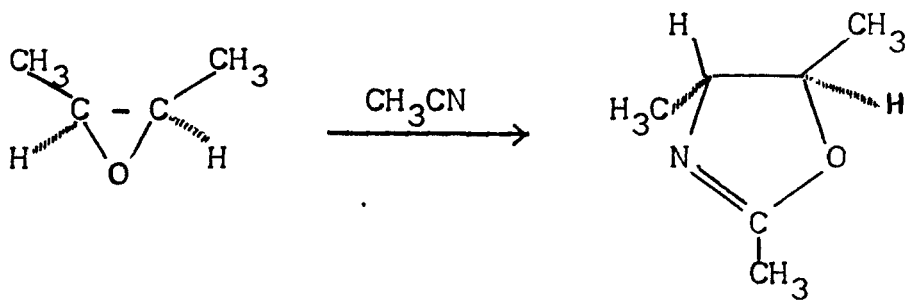
2-Oxazolines have been prepared in the author's laboratory[58] from 10,11-epoxy undecanoate (XXX) and acetonitrile, propiononitrile, benzonitrile, in presence of BF_3-etherate.

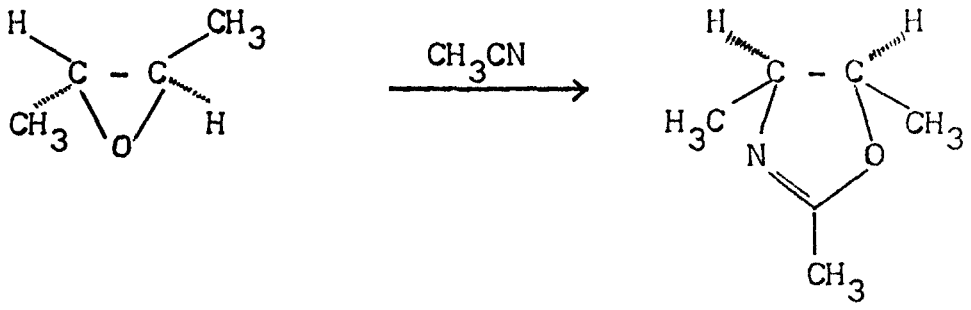


R' = $(CH_2)_8$-$COOCH_3$

R = C_2H_5, CH_3, C_6H_5.

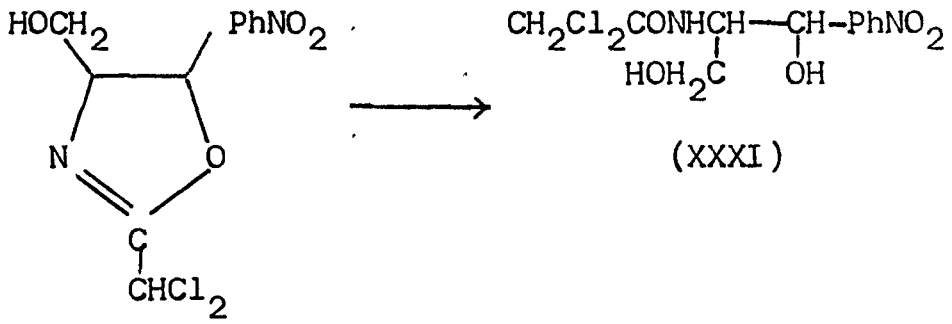
Wohl and Cannie[59] have discussed the stereochemistry of 2-oxazoline formation from the epoxide. The mechanism involves the acid catalysed ring opening of epoxides with nitriles to give 2-oxazolines. They selected 2,3-epoxybutane as substrate to study the stereochemistry of the reaction and observed that the reaction of <u>cis</u>-2,3-epoxybutane with CH_3CN gave <u>trans</u>-2,4,5-trimethyl-2-oxazoline (E) exclusively while the <u>trans</u> isomer of the substrate afforded <u>cis</u>-2,4,5-trimethyl-2-oxazoline (F) as the sole product.





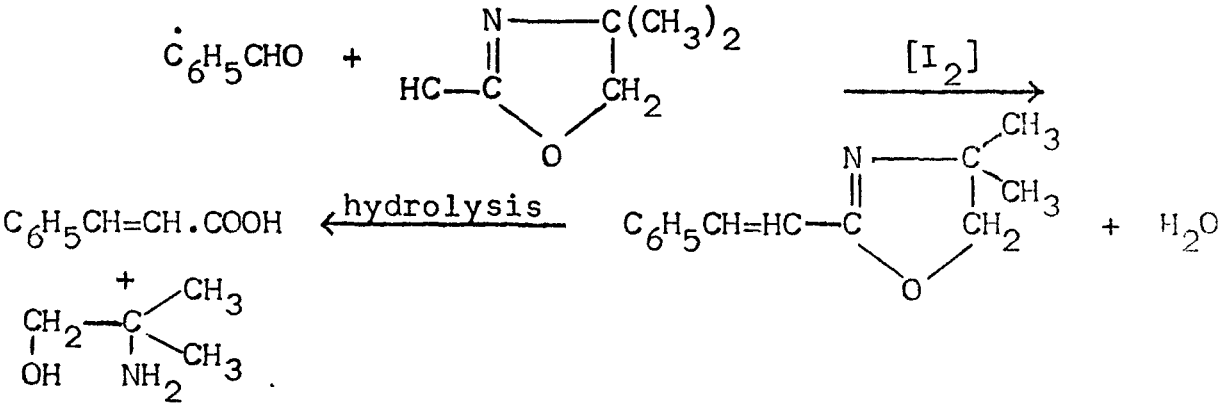
(F)

The oxazoline ring represents an interesting structure from which a number of important compounds can be prepared. An antibiotic, chloramphenicol[44] (XXXI) has been synthesised from the intermediate 2-oxazoline.

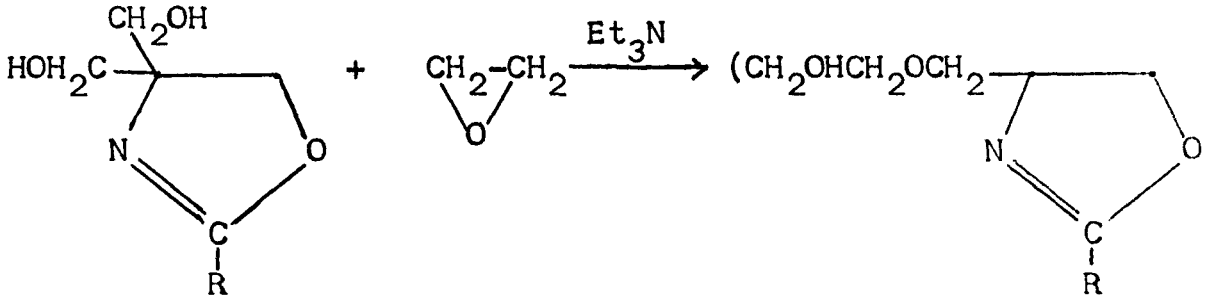


(XXXI)

Aromatic and aliphatic aldehydes also undergo reactions with 2-oxazolines and provide cinnamic acid[60] and substituted 2-oxazoline[61] (XXXII).

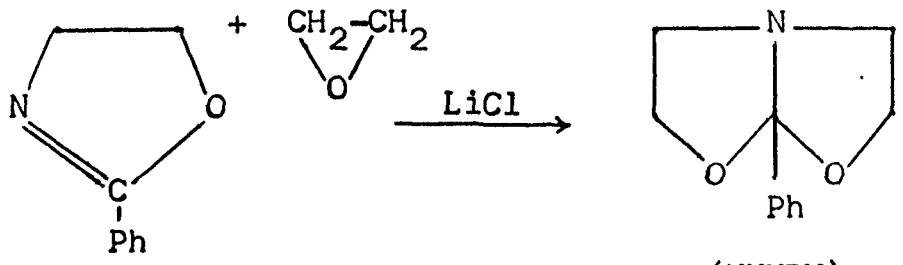


Epoxides undergo base catalysed addition with hydroxy methyl substituted 2-oxazoline to form hydroxy ethyl ether[51] or polyether depending on the ratio of epoxides to oxazoline[62] (XXXIII).



(XXXIII)

The 2-oxazoline having no active group on 4- or 5-positions on reaction with epoxide forms 1-aza-4,6-dioxabicyclo (3,3,0) octane in the presence of lithium chloride catalyst but by the reaction of ethylene oxide and 2-phenyl-2-oxazoline the product is 1-aza-5-phenyl-4,6-dioxobicyclo(3,3,0)octane[63](XXXIV).



(XXXIV)

Present Work

Long chain α,β-unsaturated fatty acids have not been studied in detail. A survey of the literature shows that the

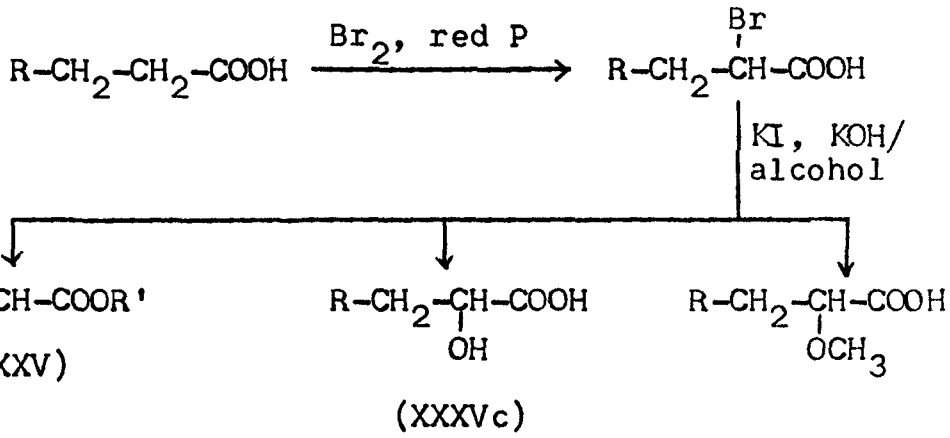
results obtained by different group of workers at different intervals of time have led to the interpretation which are conflicting as far as the mechanism and stereochemistry are concerned. Long chain α,β-unsaturated fatty acids have been a neglected part due to their non-occurrence in natural fats and their little reactivity owing to the influence of electron withdrawing carboxyl group.

We have observed that 2,3-epoxy fatty esters do not form 2-oxazolines whereas the internal epoxy fatty esters do form 2-oxazolines. The 2-oxazolines are very reactive substances These are usually readily hydrolysed to the corresponding N,β-hydroxyalkylcarboxamide[64-65] when exposed in air.

Preparation of Methyl trans-2-octadecenoic acid (XXXVa)

Methyl trans-2-octadecenoic acid was prepared[66-67] from octadecanoic acid (Scheme-6). The structure of trans-2-octadecenoic acid (XXXVa) was confirmed by elemental analysis and spectral study of its methyl ester. The compound (XXXVb) had characteristic IR absorption bands at 1730 ($-\underline{COO}CH_3$), 1650 (-CH=CH-) and 980 cm^{-1} (trans-double bond), Its NMR spectrum gave doublet of a doublet at δ 6.9 (1H, J=15 and 5 Hz) ascribable to a proton β to ester carbonyl, a doublet at δ 6.0 (1H, J=15 Hz with a small long range coupling attributed to a proton α to ester carbonyl, a multiplet at δ 2.42 ($2H, CH_2$-CH=CH)

and usual signals as observed in fatty acid esters. The coupling constant established the trans configuration of the double bond.



R = $CH_3-(CH_2)_{14}$

R'= CH_3

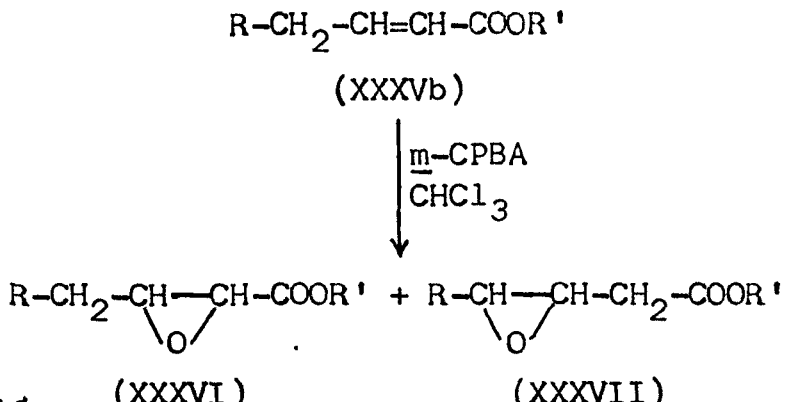
(XXXVa); R'= H

(XXXVb); R'= CH_3

Scheme - 6

Epoxidation of Methyl trans-2-octadecenoate (XXXVb)

Epoxidation of methyl trans-2-octadecenoate with m-chloroperbenzoic acid[68] showed three spots on TLC. One of which correspond to unreacted methyl ester (Scheme-7). The products were separated with the help of silica gel column chromatography.



R== $CH_3(CH_2)_{13}$ (XXXVI) (XXXVII)

R'= CH_3

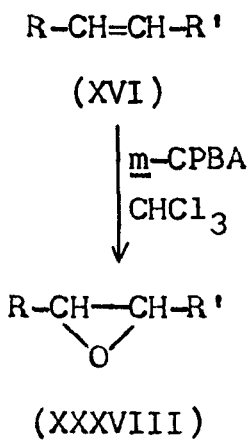
Scheme - 7

Characterisation of the Compound (XXXVI)

The compound (XXXVI), m.p.35-36 C, was characterised on the basis of co-TLC and spectral data with the authentic sample synthesised in our laboratory[69]. Its IR spectrum showed a strong absorption band at 890 cm^{-1}, characteristic for trans-epoxy group. Two partially resolved absorption bands at 1740 and 1735 cm^{-1} were attributed to the streching vibration of carbonyl function. The absorptions at 1285 and 1240 cm^{-1} were as a result of the ring breathing vibration of (C-C) and (C-O) bands and 1100 and 1175 cm^{-1} for (C-O) bond. The -CH group in the ring absorption was observed at 3000 cm^{-1}. The NMR spectrum gave signals at δ 3.72 s(3H, $-COOCH_3$), 3.01 br,s (2H, trans epoxide protons $-\underset{O}{CH}-CH-\overset{O}{\overset{\|}{C}}-OCH_3$), 1.7 br,s [28H, $(CH_2)_{14}$] and 0.88 t (3H, CH_3).

Preparation of Methyl cis-9,10-epoxyoctadecanoate (XXXVIII)

The compound (XXXVIII) was prepared from methyl cis-9,10-octadecenoate (XVI) using m-CPBA as oxidant (Scheme-8). The compound (XXXVIII) was purified by silica gel column chromatography. Its IR spectrum showed a band at 1740 cm^{-1} for ester carbonyl and the moderately intense bands at 840 and 820 cm^{-1} for cis epoxide group. The NMR spectrum showed signals at δ 2.69 m (2H, $-\underset{O}{CH}-CH-$), 2.22 m (2H, $-CH_2-COOCH_3$), 1.32 br,s [28H, $(CH_2)_{14}$] and 0.88 t (3H, CH_3)



R = $CH_3(CH_2)_7$

R'= $(CH_2)_7COOCH_3$

Scheme - 8

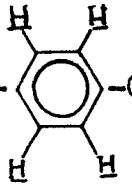
Reaction of Methyl trans-2,3-epoxyoctadecanoate (XXXVI) with Benzyl nitrile

When equimolar amounts of methyl trans-2,3-epoxyoctadecanoate (XXXVI) and borontrifluoride-ether complex were stirred with an excess of benzyl nitrile as solvent for 2 hours at room temperature, it resulted in the development of two spots on the TLC plate. After usual workup, only one product was obtained (Scheme-9).

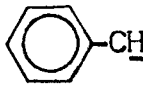
Characterisation of the solid Compound (XXXIX) m.p.61 C

The solid compound (XXXIX), m.p.61 C analysed for $C_{27}H_{43}NO_4$. The IR spectrum of this compound displayed absorption bands at 3360 (-OH), 3265 (-NH), 1730 (-COOCH$_3$), 1650 (-NHCO-) and 3040, 3000, 1600, 1490 cm^{-1} (benzene ring). The

NMR spectrum of this compound exhibited signals at δ 7.33 m

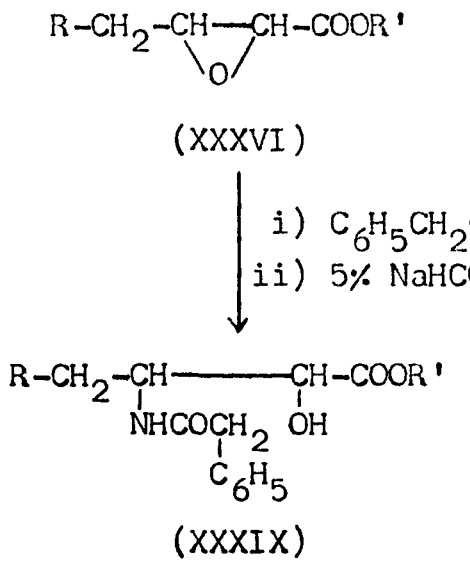


(5H, H-, -CH_2), 5.73 d (1H, CH-NH), 4.27 m (2H, CH-CH-$COOCH_3$; NH OH)

3.74 s (3H, -$COOCH_3$), 3.6 s (2H,  -CH_2-CO), 2.0 m (1H, -CH, OH

D_2O exchangeable), 1.35 br,s [28H, $(CH_2)_{14}$] and 0.87 t (3H, CH_3).

On the basis of elemental analysis and spectral data, the compound (XXXIX) was characterised as 3-benzylamido-2-hydroxyoctadecanoate



R = CH_3-$(CH_2)_{13}$

R'= CH_3

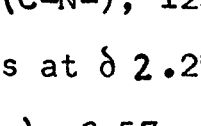
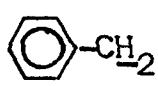
Scheme - 9

Reaction of Methyl cis-9,10-epoxyoctadecanoate (XXXVIII) with Benzyl nitrile

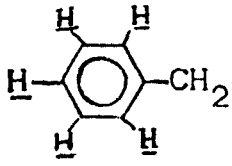
Methyl cis-9,10-epoxyoctadecanoate was reacted with benzyl nitrile in presence of borontrifluoride ether complex

(freshly distilled) in equimolar amount at room temperature for 4 hours. Examination of the final reaction mixture by TLC showed two spots. Separation by column chromatography over silica gel yielded two compounds, an oily compound (XXXX) and a semi-solid compound (XXXXI) (Scheme-10).

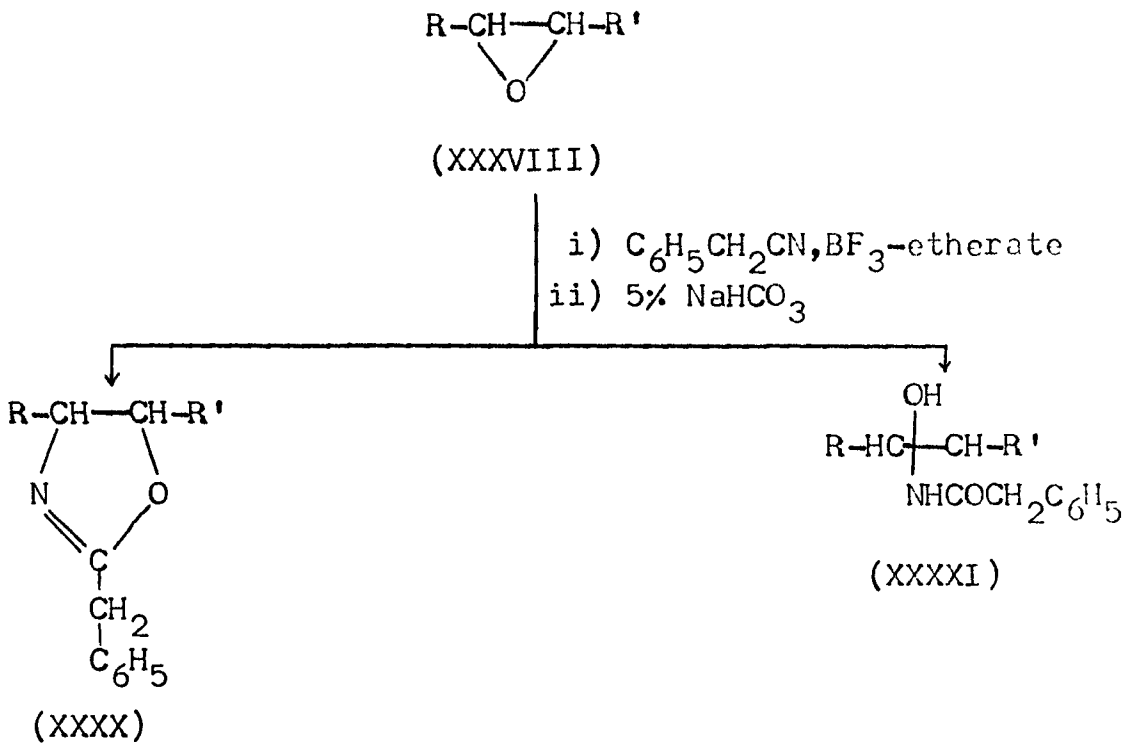
Characterisation of oily Compound (XXXX)

IR spectrum of (XXXX) exhibited absorption bands at 1750 ($-\underline{COO}CH_3$), 1665 (C=N), 1445 (C-N-), 1250 and 1160 cm^{-1}. Its NMR spectrum exhibited signals at δ 2.25 m (5H, ), 4.04 m (1H, $-\underset{O}{\underline{CH}}$), 3.88 m (1H, $-\underset{N}{\underline{CH}}-$), 3.57 s (3H, $-COO\underline{CH_3}$), 3.41 m (2H, ), 1.30 br,s [28H, $(CH_2)_{14}$] and 0.93 t (3H, CH_3). The compound (XXXX) is believed to be an isomeric mixture on the basis of mechanistic ground and formulated as 2-benzyl-4(5)-carbomethoxyheptyl-5(4)-octyl-2-oxazoline.

Characterisation of semi-solid Compound (XXXXI)

The compound (XXXI) analysed for $C_{27}H_{45}NO_4$. The IR spectrum of this compound displayed bands at 3420 (-OH), 3270 (-NH), 1730 ($-\underline{COO}CH_3$), 1630 (-NHCO) and 3030, 3000, 880 cm^{-1} were accounted for benzene ring. The NMR spectrum of (XXXXI) exhibited signals at δ 7.31 m (5H, ), 6.1 (1H, CH-NH),

4.3 m (2H, $\underline{CH}(NH)-\underline{CH}(OH)-COOCH_3$), 3.68 s (3H, $COO\underline{CH}_3$), 3.48 s (2H, $C_6H_5-\underline{CH}_2-CO$), 2.9 m (1H, $-\underline{CH}(OH)-$, D_2O exchangeable), 1.28 br,s (28H, $[\underline{CH}_2)_{14}$] and 0.97 t (3H, $-\underline{CH}_3$). On the basis of above data and mechanistic ground the compound (XXXXI) was characterised as 9(10)-benzylamido-10(9)-hydroxyoctadecanoate.



R = $CH_3(CH_2)_7$

R' = $(CH_2)_7COOCH_3$

R'' = $(CH_2)_7COOCH_3$

R''' = $CH_3(CH_2)_7$

Scheme - 10

EXPERIMENTAL

All melting points were taken in capillary tubes in an electrically heated block and are uncorrected. Infrared (IR) spectra were recorded on a Pye Unicam SP-3-100 given in cm^{-1} and usually as nujol mulls, neat, solution (CCl_4) or thin films between KBr discs. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian-A60 (60 MHz) instrument. Chemical shifts are reported as δ (ppm) relative to tetramethylsilane (TMS) using 10-15% solution in CCl_4 or $CDCl_3$. The abbreviations 's, d, m, br and t' dinote 'singlet, doublet, multiplet, broad and triplet', respectively.

Thin layer chromatography (TLC) plates were coated with silica gel G and plates were usually developed with mixture of petroleum ether, ether and acetic acid (80:20:1). TLC plates were sprayed with 20% aqueous solution of perchloric acid and charred at 110 C for 10 min. Column chromatography was carried out with silica gel (60-120 mesh) using 25-30 gm per gm of material to be separated. Elution was usually effected with petroleum ether containing increasing proportions of ether.

Commercial grade 10-undecenoic acid, 10-octene, cis-9,10-octadecenoic acid and stearic acid were used as starting materials.

Reaction of Methyl 10-undecenoate (X) with Sodium azide and Ethane nitrile

Bromine (3.2 gm, 0.02 mole) was added to a well stirred and cooled (0 C) solution of ester (X) (3.96gm, 0.02 mole) and anhydrous aluminium trichloride ($AlCl_3$, 2.68 gm, 0.02 mole) in ethanenitrile (120 ml). Within a few minutes sodium azide (NaN_3, 1.43 gm, 0.022 mole) was added in portions. The reaction mixture was allowed to attain room temperature and stirred for 5 hours and filtered. Filtrate was diluted with water, extracted with dichloromethane (100 ml x 4), washed with water, dried (Na_2SO_4) and solvent was evaporated off. The crude mixture was resolved by silica gel column chromatography. Elution with petroleum ether:ether (95:5, v/v) gave 1.15 gm (~16%) of (XI).

IR(neat) : 1740 ($-\underline{C}OOCH_3$), 670 (C-Br) cm^{-1}.

NMR($CDCl_3$) : δ 4.4-3.95 m (3H, $C\underline{H}_2$-Br and $C\underline{H}$-Br), 3.75 s (3H, $-COOC\underline{H}_3$), 2.2 m (2H, $C\underline{H}_2COO^-$), 1.3 br,s [14H, $(CH_2)_7$].

Subsequent elution with petroleum ether:ether (60:40, v/v) gave light brown oil (XII) (5.78 gm, 80%).

Methyl 11-bromo-10-(5'-methyl-1H-tetrazole)-undecanoate (XII)

Elemental Analysis

Analysis-Found : C, 46.51; H, 6.62; N, 15.36

$C_{14}H_{25}O_2N_4Br$ requires : C, 46.25; H, 6.97; N, 15.50%.

IR(neat) : 1735 ($-\underline{COO}CH_3$), 1525, 1460, 1375 (N=N, C=N), 1255, 1080, 987 (CN_4 ring), 665 (C-Br) cm^{-1}.

UV(Methanol) : λ_{max} 215 nm.

NMR($CDCl_3$) : δ 4.65 m (1H, $C\underline{H}$-N<), 3.9 s (1H) and 3.8 dist. d (J=3 Hz for CH_2-Br), 3.6 s (3H, $COOC\underline{H}_3$), 2.61 s (3H, C-$C\underline{H}_3$), 2.3 m (4H, C-9 methylene and CH_2COO^-), 1.28 br,s [12H, $(CH_2)_6$].

Mass : m/z 362/360 (M^+).

Reaction of 10-octene (XIII) with Sodium azide and Ethanenitrile

To a well stirred and cooled (0 C) solution of the compound (XIII) (2.2 gm, 0.02 mole) and anhydrous aluminium trichloride ($AlCl_3$) (2.68 gm, 0.02 mole) in ethanenitrile (100 ml) was added bromine (3.2 gm, 0.02 mole). Within a few minutes NaN_3 (1.43 gm, 0.022 mole) was added in portions to the reaction mixture at room temperature for 4.5 hours. The reaction mixture was worked up as described above and the residue chromatographed over silica gel. The first elution with petroleum ether yielded a liquid compound (XIV) (0.7 gm, 15%).

IR(neat) : 668 (C-Br) cm^{-1}.

NMR : δ 4.42-3.92 (3H, $C\underline{H}_2$-Br and $C\underline{H}$-Br), 1.25 br,s [1OH, $(CH_2)_5$], 0.9 dist. t (3H, CH_3).

Further elution with petroleum ether:ether (65:35, v/v) gave an oil (XV) (4.5 gm, 82%).

1-Bromo-2-(5'-methyl-1H-tetrazole)-octane (XV)

Elemental analysis

Analysis-Found : C, 44.1 ; H, 6.8 ; N, 20.25

$C_{10}H_{19}N_4Br$ requires : C, 43.66; H, 6.95; N, 20.36%.

IR(neat) : 1525, 1455, 1380 (C=N, N=N), 1255, 1088, 985 (CN_4 ring), 665 (C-Br) cm^{-1}.

UV(Methanol) : λ_{max} 215 nm.

NMR($CDCl_3$) : δ 4.71 m (1H, $C\underline{H}$-N<), 3.91 s (1H) and 3.81 dist. d [1H, J=3 Hz (CH_2-Br)], 2.61 s (3H, C-$C\underline{H}_3$), 2.10 m (2H, C-3 methylene), 1.28 br,s [8H, $(CH_2)_4$], 0.88 t (3H, CH_3).

Mass : m/z 277/275 (M^+).

Reaction of Methyl cis-9,10-octadecenoate (XVI) with Sodium azide and Ethane nitrile

In a similar manner using the conditions described above, a mixture of compound (XVI) (5.92 gm, 0.02 mole), anhydrous $AlCl_3$ (2.68 gm 0.02 mole), bromine (3.2 gm, 0.02 mole) and NaN_3 (1.43 gm, 0.022 mole) in ethanenitrile (130 ml) was stirred for 6 hour. After work up with dichloromethane (100 ml x 4), the combined extracts were washed with water, dried (Na_2SO_4) and the solvent was evaporated off. The residue was chromatographed over silica gel. Elution with petroleum ether:ether (95:5, v/v) gave (XVII) (1.65 gm, 18%).

IR(neat) : 1735 ($-\underline{C}OOCH_3$), 665 (C-Br) cm^{-1}.

NMR($CDCl_3$) : δ 4.21 m (2H, 2xCH-Br), 3.65 s (3H, $COO\underline{C}H_3$), 2.2 m (2H, CH_2COO^-), 1.3 br,s [26H, $(CH_2)_{13}$], 0.9 dist. t (3H, CH_3).

Further elution with petroleum ether:ether (60:40, v/v) afforded (XVIII) a light brown oil (6.90 g, 75%).

Methyl threo-9(10)-bromo-10(9)[5'-methyl-1H-tetrazole]octadecanoate (XVIII)

Elemental Analysis

Analysis-Found : C, 54.78; H, 8.50; N, 11.95

$C_{21}H_{39}N_4O_2Br$ requires : C, 54.90; H, 8.55; N, 12.20%.

IR(neat) : 1755 ($-\underline{COO}CH_3$), 1535, 1465, 1375 (C=N, N=N), 1260, 1082, 985 (CN_4 ring), 665 (-C-Br) cm^{-1}.

UV(Methanol) : λ_{max} 215 nm.

NMR($CDCl_3$) : δ 4.49 m (2H, C-9 and C-10 methine protons), 3.7 s (3H, $-COOC\underline{H}_3$), 2.59 s (3H, $C-C\underline{H}_3$), 2.21 m (4H, CH_2COO^-), 1.29 br,s [24H, $(CH_2)_{12}$], 0.87 dist. t (3H, CH_3).

Mass : m/z 461/459 (M^+).

Reaction of (XII), (XV), (XVIII) with Sodium ethoxide

As a general method the tetrazole (XVII, XV, XVIII) 0.005 mole each were taken separately in 1% sodium ethoxide (50 ml) and maintained at 60 C for 2 hours. The reaction mixtures was cooled, diluted with water, acidified with a few drops glacial acetic acid and extracted with ether (40 mlx4). Combined diethyl ether extract was washed with water and finally dried over Na_2SO_4. Evaporation of the solvent furnished the corresponding dehydrobrominated compounds (XIX, XX, XXI) in quantitative yield. The spectral values of each compound are detailed as under.

Methyl 10-(5'-methyl 1H-tetrazole)-undec-10-enoate (XIX)

IR(nujol) : 1735 ($-\underline{COO}CH_3$), 1658, 922 (C=C), 1525, 1440, 1380 (C=N, N=N), 1271, 1085, 980 (CN_4 ring) cm^{-1}.

UV(Methanol) : λ_{max} 210 nm.

NMR($CDCl_3$) : δ 5.4 dist. t (1H, J=1 Hz), 5.21 s (1H, CH_2=C<), 3.58 s (3H, $COOCH_3$), 2.58 s (3H, >C-CH_3), 2.3 m (4H, CH_2-COO^-), 1.28 br,s [12H, $(CH_2)_6$].

2-(5'-Methyl 1H-tetrazole)-octa-1-ene (XX)

IR(neat) : 1658, 915 (C=C), 1520, 1445, 1380 (C=N, N=N), 1275, 1088, 987 (CN_4 ring) cm^{-1}.

UV(Methanol) : λ_{max} 210 nm.

NMR($CDCl_3$) : δ 5.4 dist. t (1H, J=1 Hz and 5.29 s, 1H for CH_2=C<), 2.54 s (3H, >C-CH_3), 1.28 br,s [10H, $(CH_2)_5$], 0.88 dist. t (3H, CH_3).

Methyl 9(10)-[5'-methyl 1H-tetrazole]-octadeca-(9E)-enoate (XXI)

IR(neat) : 1740 ($\underline{COO}CH_3$), 1515, 1440, 1380 (C=N, N=N), 1270, 1080, 980 (CN_4 ring), 1670, 885 (C=C) cm^{-1}.

UV(Methanol) : λ_{max} 210 nm.

NMR($CDCl_3$) : δ 5.88 (triplets of triplet, J=7.5 Hz and 1 Hz, -CH=C<), 3.62 s (3H, $COOCH_3$), 2.45 s (3H, >C-CH_3) 2.3 m (4H, CH_2COO^-), 1.28 br,s [24H, $(CH_2)_{12}$], 0.87 dist. t (3H, CH_3).

Preparation of Methyl trans-2-octadecenoate (XXXVb)

Dry bromine (50 ml) was added dropwise at 90°C in a period of 7 hours to a well stirred mixture of stearic acid (100 gm) and red phosphorus (4.6 gm). The mixture was vigorously stirred during the addition of bromine by using a mercury sealed stirrer. Heating was continued for 24 hours and the cooled solution was poured into cold water and left overnight. The solid product was filtered, taken up in ether, washed successively with 10% aqueous solution of sodium bicarbonate ($NaHCO_3$). The 2-bromo acid obtained after evaporation of the solvent was heated under reflux with powdered potassium iodide (96 gm) in 95% ethanol (700 ml) for 6 hours. To the cooled solution, potassium hydroxide (64 gm) was added and the contents refluxed for another 4 hours. Most of the alcohol was evaporated in vacuo and the residue diluted with water, acidified with hydrochloric acid (dilute) and extracted with ether. The combined ether extract were washed with water and dried over anhydrous sodium sulphate. After evaporation of the solvent, a mixture of α,β-unsaturated, 2-hydroxy and 2-ethoxy acids were obtained.

The 2-hydroxy acid (XXXVc) was separated from α,β-unsaturated acid as copper chelate by treatment with cupric acetate in acetic acid and ethanol. The remaining two fractions obtained after removal of 2-hydroxy acid were separated by silica gel column chromatography to furnish the individual components.

Elution with petroleum ether:diethyl ether (94:6; v/v) gave pure α,β-unsaturated acid as a colourless compound, yield ~52.0%; crystallisation achieved by petroleum ether-ethanol (75:25, v/v). The trans-2-octadecenoic acid on acid catalysed esterification yielded its corresponding ester (XXXVb)

Methyl trans-2-octadecenoate (XXXVb) m.p.58-59 C

Elemental analysis

Analysis-Found : C, 76.52; H, 12.9

$C_{18}H_{34}O_2$ requires : C, 76.52; H, 12.9%.

IR(nujol) : 1730 ($\underline{C}OOCH_3$), 1650 (C=C) and 980 (trans-olefin) cm^{-1}.

NMR(CCl_4) : δ 6.9 d.d (J=15 Hz and 5 Hz, 1H, β to ester carbonyl), 6.0 d (J=15 Hz, 1H, with a small long range coupling, trans-olefinic proton [α- to ester carbonyl)], 3.71 s (3H, $COOC\underline{H}_3$), 1.26 br,s (chain CH_2), 0.28 t (3H, CH_3).

Preparation of Methyl 2,3-epoxyoctadecanoate (XXXVI)

Reaction of m-chloroperbenzoic acid (m-CPBA) with methyl trans-2-octadecenoate (XXXVb) was carried out by following the procedure of Gunstone and Jacobsberg[64], as adopted in author's laboratory[65]. To the solution of methyl ester (2 gm)

in chloroform (25 ml), m-CPBA (6 gm) in chloroform (25 ml) was added with shaking. The volume of chloroform was increased to 200 ml. The mixture was kept at room temperature for 12 days and examined by TLC.

The mixture was washed with 5% aqueous sodium bicarbonate to remove m-CPBA and dried over anhydrous sodium sulphate. Direct TLC showed spots corresponding to unreacted methyl ester and for epoxy ester. The product (1.80 gm) was chromatographed over a column of silica gel (30 gm). Elution with petroleum ether gave unreacted methyl trans-2,3-octadecanoate (XXXVa) (1.1 gm; 61.11%). Subsequent elution with a mixture of petroleum ether:ether (90:10, v/v) gave methyl trans-2,3-epoxyoctadecanoate (XXXVI) (34.4%). When the same reaction was carried out with excess of m-CPBA, afforded 68% of (XXXVI). The melting points, combustion data and spectroscopic behaviour of methyl trans-2,3-epoxyoctadecanoate are given below.

Methyl trans-2,3-epoxyoctadecanoate (XXXVI) m.p.42-43 C

Elemental analysis

Analysis-Found : C, 73.00; H, 11.5

$C_{18}H_{36}O_3$ requires : C, 73.03; H, 11.61%.

IR(nujol) : 1750, 1735 ($-\underline{C}OOCH_3$), 1285, 1240 (C-C and C-O ring breathing vibration), 1100, 1175 (C-O) and 890 (trans-epoxy group) cm^{-1}.

NMR(CCl_4) : δ 3.72 s (3H, $COOC\underline{H}_3$), 3.01 br,s (2H, -C<u>H</u>—C<u>H</u>- epoxide), 1.7 br,s [28H, $(CH_2)_{14}$], 0.88 t (3H, CH_3).

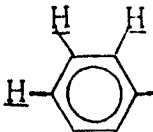
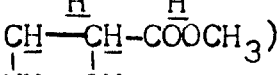
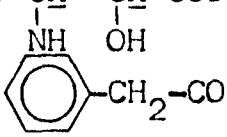
Reaction of Methyl 2,3-epoxyoctadecanoate (XXXVI) with Benzyl nitrile

To a mixture of equimolar amounts of epoxide (XXXVI) (1.0 gm, 0.003 mole) and boron trifluoride ether complex (1 ml, 0.003 ml), 6 ml benzyl nitrile was added and the whole mixture stirred at room temperature for 4 hours. The course of reaction was monitored by TLC plate. The mixture was poured into aqueous sodium hydrogen carbonate (5%) and dichloromethane extract was washed with water and dried over anhydrous sodium sulphate. The removal of solvent gave a viscous oil which showed two distinct spots on TLC plate.

Oily reaction mixture was chromatographed over silica gel (20 gm) and eluted with petroleum ether:ether (95:5, v/v). The purity of eluted material was checked by TLC plate. After evaporation of eluent, a solid compound (XXXIX) 80% m.p.61 C was obtained.

Methyl 3-benzylamido-2-hydroxyoctadecanoate (XXXIX)

IR(KBr) : 3360 (-OH), 3265 (-NH), 1730 ($C\underline{O}OCH_3$), 1650 (-NHCO) and 3040, 3000, 1600, 1490 (benzene ring) cm^{-1}.

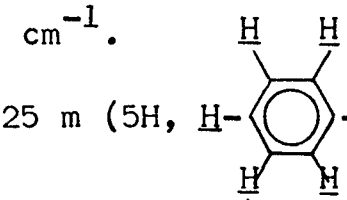
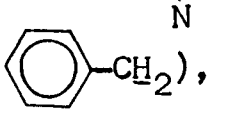
PMR($CDCl_3$) : δ 7.33 m (5H, ), 5.73 d (1H, CH-NH), 4.27 m (2H, ), 3.74 s (3H, $COOCH_3$), 3.6 s (2H, ), 2.0 m (1H, CH, OH, D_2O exchangeable), 1.35 br,s [28H, $(CH_2)_{14}$], 0.87 t (3H, CH_3).

Reaction of Methyl cis-9,10-epoxyoctadecanoate (XXXVIII) with Benzyl nitrile

Equimolar amount of epoxide (XXXVIII) (1 gm, 0.003 mole) and boron trifluoride-ether complex (1 ml, 0.003 mole) was allowed to react with 6 ml of benzyl nitrile and the mixture was stirred at room temperature for 4 hours. The progress of reaction was monitored by TLC plate. The reaction mixture was washed with 5% aqueous sodium carbonate and the dichloromethane extract was washed with water and dried over anhydrous sodium sulphate. The removal of solvent gave an oil which showed two distinct spots on TLC plate. The oily reaction mixture (1 gm) was chromatographed over silica gel column (20 gm) and elution with petroleum ether:ether (90:10, v/v) gave compound (XXXX) 40%.

2-Benzyl-4(5)-carbomethoxyheptyl-5(4)-octyl-2-oxazoline (XXXX)

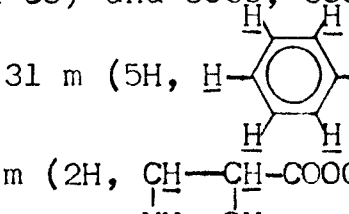
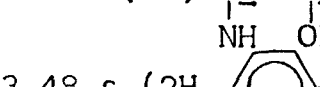
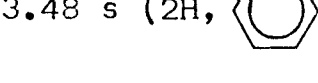
IR(neat) : 1750 ($\underline{C}OOCH_3$), 1665 (C=N), 1445 (C-N), 1250 and 1160 cm^{-1}.

NMR($CDCl_3$) : δ 2.25 m (5H, ), 4.04 m (1H, ), 3.88 m (1H,), 3.57 s (3H, $-COOC\underline{H}_3$), 3.41 m (2H, ), 1.30 br,s [28H, $(CH_2)_{14}$], 0.93 t (3H, CH_3).

Subsequent fractions collected by elution with petroleum ether:ether (60:40, v/v) gave a semi-solid compound (XXXXI) (60%).

9(10)-Benzylamido-10(9)-hydroxyoctadecanoate (XXXXI)

IR(nujol) : 3420 (-OH), 3270 (-NH), 1730 ($\underline{C}OOCH_3$), 1600 (-NH-CO) and 3030, 3000, 880 (benzene ring) cm^{-1}.

NMR($CDCl_3$) : δ 7.31 m (5H, ), 6.1 d (1H, CH-N<u>H</u>), 4.3 m (2H, ), 3.68 s (3H, $COOC\underline{H}_3$), 3.48 s (2H, ), 2.9 m (1H,  , D_2O exchangeable), 1.28 br,s (chain-CH_2 signal) and 0.97 t (3H, CH_3).

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